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THE QUANTITATIVE DETERMINATION OF ARSENIC, BY THE BERZELIUS-MARSH PROCESS, ESPECIALLY AS APPLIED TO THE ANALYSIS OF WALL-PAPERS AND FABRICS.[1]

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The original method of Marsh[2] was published in 1836, and in the following year Berzelius[3] proposed the modification which couples his name with that of Marsh. It seems to have escaped notice, at least I can find no mention of the fact, that Berzelius also suggested the quantitative application of the method. He proposed to place some pieces of copper in the reduction-tube, and, after weighing tube and copper, to heat and pass the arsenical gas through. The copper would further the reduction of the arseniuretted hydrogen, and thus the arsenic might be collected and weighed. Wöhler,[4] in 1861, proposes essentially the same method, but heats the tube in two places, at the copper which he uses in the form of a spiral, two inches long, and also just behind the copper, so that whatever gas escapes decomposition by the first heating may be decomposed by the copper. The first practical application of this method seems to have been made by Gautier,[5] in 1876, in the estimation of arsenic contained in tissues.

[1] From the Proceedings of the American Academy of Arts and Sciences. Communicated by the Author.

[2] Edin. Philos. Journ. **21**, 229.

[3] Berzelius, Jahresb. **17**, 191.

[4] Mineral-analyse, p. 232.

[5] Ann. d'Hygiène publ. et de Méd. légale, 1876, p. 136; also Bull. de la Soc. Chim. [2] **24**, 250.

He omits the copper spiral, but heats the reduction-tube by a layer of charcoal 20 to 25 cm. in length. To determine the arsenic deposited, he weighs the tube, dissolves out the mirror by nitric acid, and, after drying, weighs again. Crommydis,[1] a year later, follows Gautier's method in a similar research.

Chittenden and Donaldson,[2] in 1881, investigated this method with very satisfactory results, and suggested the improvements which were necessary for its adoption as a trustworthy analytical method. Their process has found its way into the text-books, and needs no explanation here. I note its use by Hubbard[3] in 1882, and Prescott[4] in 1886, and undoubtedly many others have employed it in toxicological work. . It seems remarkable, therefore, that the previous application of the process to quantitative work should have escaped the attention of Kühn and Saeger,[5] as well as Polenske,[6] to whom they refer as the first to propose the method. Kühn and Saeger's article, published a few months ago, contains nothing new; but as the paper of Polenske is inaccessible to me, I cannot say what modification he may have introduced.

I need not refer here to the numerous quantitative methods which depend on the reduction by nascent hydrogen and absorption of the arseniuretted hydrogen by argentic nitrate, the eventual determination of the arsenic being made from the silver solution in a variety of ways. These methods form a class by themselves, and cannot be included in the Berzelius-Marsh process.

All methods for the estimation of arsenic are open to a common objection; they do not allow the estimation of minimal, or even, with accuracy, of small amounts. It happens so often that a small amount of arsenic must remain unestimated, because unweighable, and only an approximation to the real quantity can be made.

In the qualitative analysis of wall-papers and fabrics by the Berzelius-Marsh method, much confusion results from the careless manner of reporting the amount of arsenic which makes its appearance in the reduction-tube. The reports, "trace," "small amount," "large amount," are usually made without reference to any standard mirrors, time of heating the reduction-tube, or, in

[1] Bull. de la Soc. Chim. [2] **25**, 348.

[2] This Journal **2**, No. 4; Chem. News **43**, 21; Moniteur Scient. de Paris, 1881, p. 227.

[3] Physician and Surgeon, Ann Arbor, **4**, 348; also Contributions from the Chem. Lab. Univ. Mich., Vol. I, Part I, p. 12.

[4] Chem. News **53**, 79.

[5] Ber. d. chem. Ges. **23**, 1798.

[6] Arb. a. d. kais. Gesundheitsamt, Bd. V, Heft 2 (1889).

many cases, to the amount of substance taken for analysis. On account of the want of a definite quantitative method which could be easily applied to wall-papers and fabrics, there have been some propositions for a rough quantitative determination, which should serve as a control as to whether the substance contained more or less than a prescribed amount. The Swedish law[1] of 1883, for instance, though not using the Berzelius-Marsh method, prescribes that "440 sq. cm. of the article . . . by reduction with potassic cyanide and sodic carbonate, shall not produce more than a partially opaque mirror in a glass tube of 1.5 to 2 mm. inner diameter." Thoms,[2] in 1883, proposes as a means of control that the results from 100 sq. cm. of paper should be divided into four grades: "strongly arsenical," "arsenical," "traces," and "free." If, when the apparatus has been running ten minutes after the introduction of the solution to be tested, a deposit is obtained no larger than that corresponding to what is produced by 0.1 mgr. of arsenious oxide under similar conditions, the paper may be considered to contain a "trace," and need not be rejected.

A committee of the National Health Association of Great Britain, consisting of Messrs. Bartlett, Heisch, and De Chaumont,[3] suggested, in 1883, that a paper should be considered non-arsenical if, after being treated by a modification of the Berzelius-Marsh method devised by them, it failed to give a mirror in a tube of one-eighth inch internal diameter (about 3.3 mm.) sufficient to cut off at any point a black line of a certain thickness ("thick rule, 8 to pica") on a white ground.

All this is very crude, yet, without a means of easily estimating the amount of arsenic present, it might answer until the exact determination was called for.

The length of time necessary for any of the quantitative methods precludes their use by analysts, especially when, as is generally the case, the quantitative determination is not of especial importance. If we attempt to apply the gravimetric Berzelius-Marsh method to the analysis of wall-paper, we are met, not only by the amount of time necessary for the complete deposition of the arsenic mirror, but by the large amount of paper that must be taken, or,

[1] Correspondence between the English and other Governments respecting the Presence of Arsenic . . . in Wall Papers and Textile Fabrics. Commercial, No. 40 (1883).

[2] Ref. Fres. Zeitschr. **22**, 474, from Ber. d. landw. chem. Vers. u. Samencontrolstat. zu Riga, 1883.

[3] Brit. Med. Jour. 1883, p. 1218.

if the proportion of arsenic is very small, the unwieldy amount. Added to this is the necessity for a delicate balance, and also the error in weighing small mirrors of arsenic.

A method is therefore desirable which will allow us to estimate minimal amounts of arsenic, and, in such analyses as that of wall-paper, will give an approximate idea of the amount present without requiring more time than that needed for the proper conduct of the ordinary Berzelius-Marsh method.

The process which is described in the following pages was suggested by Professor H. B. Hill, of Cambridge, about five years ago, and has been in use in that laboratory and others with excellent success. The proof of the availability of the method was undertaken by me, but, owing to numerous interruptions, the completion of the analytical work has been delayed until now.

The method consists, briefly, after getting the arsenic from a measured amount of paper or fabric into solution, in the comparison of the mirror obtained from an aliquot part of the solution with a series of standard mirrors obtained from known amounts of arsenious oxide. No method founded on exactly this principle has ever been fully described, though Otto[1] gives cuts of mirrors obtained from known amounts of arsenious oxide, with which some analysts may have compared their mirrors. Selmi,[2] in 1880, states that he is able to approximate to fractions of a milligram by comparing the mirrors with those obtained from the following amounts: one-twentieth, one-fiftieth, one-hundredth, and one-two-hundredth part of a milligram. Thoms, as stated above, compares his "traces" with a mirror obtained from one-tenth of a milligram, and says that the mirror can be kept any length of time as a comparison standard. Blyth[3] also suggests a comparison of mirrors.

I give in detail the method as I have used it in the analysis of wall-paper, making references to the analytical and experimental work which follows.

The measurement of the paper is governed by (*a*) the quantity of arsenic present, which may sometimes be judged by the color, or by the rough test of the odor from the burning paper, and (*b*) by the character of the paper; *i. e.* whether a plain color, a small or large figure. I have used 25 sq. cm., 50 sq. cm., and usually 100 sq. cm. As patterns for cutting, thin plates of glass[4] may be

[1] Graham-Otto-Michaelis, Lehrbuch, **2**, 2, 520.
[2] Gazz. Chim. Ital. **10**, 435.
[3] Poisons, their Effect and Detection, 1884, p. 534.
[4] Dr. Charles Harrington.

used, on which are marked the dimensions. The advantage of the glass is, that the figure of the paper may be seen while the paper is being cut, and also, that, by washing or wiping the glass after each cutting, any danger of contamination by adhering particles from a previous arsenical paper may be avoided. I have used but one plate for 25 sq. cm. (5 × 5); for 50 sq. cm., three (5 × 10, 4 × 12.5, and 2 × 25); and for 100 sq. cm., five (10 × 10, 5 × 20, 4 × 25, 8 × 12.5, and 2 × 50); such a number allowing the variety in cutting that different papers necessitate.

The paper, cut into small pieces, is placed in a glazed porcelain dish and moistened with 1 to 5 cc., according to the amount of paper taken, of strong sulphuric acid (sp. gr. 1.8) to which has been added about one-thirtieth of its volume of strong nitric acid (Appendix, 2. *e*). The paper and acid are stirred with a thick glass rod until the paper has absorbed the acid, and the dish is then placed on a ring and heated by a low flame, the mixture being stirred continually, until the paper is thoroughly charred (App. 1). This may be determined by the dry "crumbly" appearance, and by the amount of fuming, it being necessary to heat until the nitric acid is expelled. Usually, the first heating is enough, as even if a trace of nitric acid is left, it does no harm (App. 2. *f*); yet, if one has reason to think that considerable nitric acid is held back, it is best, after cooling, to add a few cubic centimeters of water, and heat again until the fumes of sulphuric acid appear. On cooling, the "char" is moistened with a few drops of water, and then about 5 cc. of water are added. The mass is triturated with the thick rod until all lumps are thoroughly broken up, heated to boiling to expel sulphur dioxide (App. 5. *d*) and filtered hot (App. 3).

Filtration of the Extract.—In filtering, time is saved and greater accuracy assured by using a filter-pump, and for filtration I have found most convenient a side-neck test-tube of 25 to 30 cc. capacity. This is fitted with a rubber cork through which passes a small funnel, the end reaching just below the side tubulus of the test tube. With the tubulus is connected the pump, and in order to prevent accidental contamination of the tubulus (through which the extract is afterwards poured into the Marsh apparatus), I use a connecting glass tube, which may be rinsed before and after each filtration. This tube is a small U tube not over 25 cm. in total length, with two bulbs blown in the lower part of the U. The

filter-paper is of small diameter, not over 8 cm., and the lot should be tested for arsenic previous to cutting the round filters. As a strengthening cone at the apex will be found convenient for this, as well as for other filtrations, a square piece of cheese-cloth laid under the paper and folded with it.

After filtering, the char is washed with small quantities of hot water until the filtrate and washings fill the test-tube. The extract, after cooling, is ready for weighing or measuring, and introduction into the apparatus.

The Apparatus.—Two points will have been noticed in working with the ordinary form of generating flask: the time required for displacement of the air, and the impossibility of governing the evolution of hydrogen during the analysis. The latter objection is partially remedied by some such contrivance as that of Lehmann[1] or of Blondlot,[2] both of whom regulate the current by raising or lowering the zinc by a glass rod working through the cork of the flask. Chittenden and Donaldson[3] regulate the evolution by the successive use of acids of increasing strength. Both difficulties are, however, obviated by the use of a constant hydrogen-generator by which the air of the flask may be swept out and the flow of the hydrogen controlled, thus assuring the uniform rate of deposition of the arsenic, on which the success of the process as a quantitative one largely depends. This idea of a constant generator was apparently first proposed by Verryken,[4] and has been used also in 1888 by Wolff[5] in a modification of Bloxam's electrolytic method.[6] Any form of generator can of course be used. To the delivery-tube is attached a distributing tube, which may be two-way or three-way, according to the number of reduction-flasks used. For two flasks an ordinary Y-tube suffices, each end of the Y being fitted with a thick rubber connecting tube and a screw clamp, so that the supply of hydrogen may be shut off entirely or controlled for each flask. The reduction-flask is a wide-mouthed bottle of about 75 cc. capacity, fitted with a rubber stopper pierced with three holes. Through one hole passes a right-angled tube reaching to the bottom of the flask, the other

[1] Pharm. Zeitschr. f. Russland, 1888, **27**, 193.
[2] Mémoires de la Soc. Roy. de Sci., Lett. et Arts de Nancy, 1845.
[3] Loc. cit.
[4] Ref. by Dragendorff, Ermittelung von Giften, 1876, pp. 337 and 317, to Jour. de Pharm. d'Anvers, 1872, pp. 193 and 241.
[5] Ztschr. analyt. Chem. **27**, 125.
[6] Ibid.; also Blyth, loc. cit., p. 533.

end being connected with the distribution-tube of the generator. Through the second hole passes the right-angled delivery-tube, reaching just below the rubber cork. The third hole serves for the introduction of acid and extract. Through it passes to the bottom of the flask a tube with the bore at the lower end somewhat reduced by melting.[1] In the top of this tube is set a very small funnel.

To the delivery-tube of the reduction-flask is attached by a rubber stopper a straight bulb drying tube filled with fused calcic chloride (App. 5. *a*), and to the drying tube is connected by a short thick rubber tube the reduction-tube, which should be of the hardest and best quality of Bohemian glass (App. 5. *b*), and of as uniform bore as possible, about 7 mm. inside and 8 mm. outside diameter. It should be drawn out before a small blast-lamp flame to as nearly as possible definite bore, which ought to be from 1.5 mm. to 2 mm. at the place of deposition of the arsenic mirror. The finely drawn tube is bent slightly upward, and sealed at the end.

The Reagents (App. 4).—The zinc and sulphuric acid used in the apparatus must be *strictly* free from arsenic, and one should not feel satisfied of their purity unless a stream of hydogen from the generator, led through the heated tube for several hours, fails to give the slightest deposit. The granulated zinc used in the generator is best of comparatively large size, while that used in the reduction-flasks should be quite fine-grained. The acid should have a concentration of one part strong acid (1.82 sp. gr.) to eight parts of water, though a more dilute acid can often be used.

The Course of Analysis.—In the reduction-flask is placed a small quantity, not over three grams, of zinc, and the apparatus is connected together. Tightness must be assured, and can be tested for, if the tip of the reduction-tube is sealed, by adding through the small funnel a few drops of acid. If these do not fall, the tip of the tube is broken off, leaving an opening of not more than 1 mm. diameter, and then about 20 cc. of acid are added. The hydrogen is now turned on from the generator, and, after expulsion of the air, lighted, and the flame turned down to a height of 1 to 2 mm. The evolution of hydrogen should be kept at this rate during the reduction of the arsenical solution. Often it is not necessary to use the generator during the reduction, as the evolution from the reduction-flask is sufficiently rapid. If it

[1] That the fluid introduced may not carry any air with it into the flask.

slackens, the generator may be used again, and indeed it is generally necessary to use it toward the close of the reduction. It may happen, on account of too strong acid or increased action after introduction of the extract, that the evolution is too rapid, and the flask becomes heated (App. 5. *c*). To obviate this, the flask may be set in a vessel fitted with an exit tubulus, and filled with cold water, which can be drawn off and replaced when necessary without disturbing the apparatus. An ordinary crystallising dish with a siphon would answer the purpose.

Shortly after (App. 5. *e*) lighting the hydrogen, the lamp is placed under the heating place and the apparatus tested for absence of arsenic for such length of time as the circumstances direct. In ordinary analyses of wall-paper, I allow 15 to 20 minutes' free run before adding the extract.

The lamp should give a large, clearly defined flame (App. 5. *f*), and should heat the tube with its oxidising flame only. An iron cone may be used for increased draught, but not an iron or glass cylinder, for the greater radius of heat given by the latter tends to throw the mirror farther along the tube, and to deposit it irregularly. A convenient rest for the reduction-tube is made by soldering three stout copper wires to an old binding-screw or post, curving the ends to fit the tube and branching them out, so that the tube lies flat in the curved ends. The binding screw travels vertically on a brass rod melted into a flat, heavy piece of lead, or screwed into the base of an old Bunsen burner.

When the apparatus is found free from arsenic, the extract is added. Previous to this it has been measured or weighed, preferably the latter. The test-tube having its weight marked on it, the weight of the extract is quickly determined. Weighings can be made on a balance sensitive to fifty milligrams, which is enough for all practical purposes.

A few drops of the extract are at first added. If no mirror appears in three or four minutes, one-eighth to one-quarter of the rest may be added, and if in five minutes more there is no mirror, the whole of the extract may be introduced. This cautious addition is necessary in order not to obtain too large a mirror, else a difficulty in estimation might arise, or a new determination might have to be made. A twenty-five minute run is sufficient for the deposition of all the arsenic when the size of the mirror formed in the first fifteen minutes is not larger than that corresponding to 0.05

mgr. of arsenious oxide. If the mirror forming is likely to be larger than this, it is better, after weighing, to start another mirror with another portion of the extract, than to wait for the complete deposition of a mirror which may be too large for comparison with the standards.

The set of standard mirrors is made as follows: One gram of arsenious oxide, purified by repeated sublimation, is dissolved with the aid of a little sodic bicarbonate (free from arsenic), and, after acidification with dilute sulphuric acid, is made up to a litre. Of this standard solution (I.), containing 1 mgr. As_2O_3 to 1 cc., ten cc. are taken and made up to a litre, giving the standard solution (II.) containing 0.01 mgr. to 1 cc. Of this solution, 1 cc., 2 cc., 3 cc., etc., are carefully measured from a burette and introduced into the reduction-flask of the apparatus, giving the mirrors corresponding to the same number of hundredth-milligrams. It is necessary to make two or more mirrors of the lower amounts, as, even with careful drawing, the cross-sections of the deposition-tubes differ, so that the appearance of the mirror from the same amount of arsenic varies, and the variation is more marked as the mirrors decrease in size. Then, for greater convenience in interpolation, mirrors corresponding to the half-hundredths may be made, so that the set which I use contains the following amounts: 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, and 0.06. Above 0.06 the difference between the mirrors is so hard to estimate with accuracy that it is of no advantage to make any above 0.06. Yet in the set which I have photographed, and which is shown in the plate, the following are added for comparison: 0.07, 0.08, 0.09, 0.10.

When the set is not in use, it should be kept in the dark, and *at no time* be exposed to direct sunlight. Although the tubes be sealed, yet there is sufficient air inside to cause a rapid oxidation in direct sunlight, especially with the lower amounts, and a film of arsenious oxide results. By observing this precaution, the set can be kept a long time without alteration.

The readings of the mirrors are far sharper by transmitted than by reflected light, and comparison should always be made by the former. For this purpose I use, at the suggestion of Professor Hill, a small tin box painted black on the inside and outside, and similar in shape and construction to the old-fashioned stereoscopic camera. The height of the box is 20 cm.; width, 7.5 cm.; length at top, 10 cm.; length at bottom, 15 cm. The bottom is open,

while the top is covered, and fitted with two eyeholes, 2 cm. in diameter and 4 cm. apart. The set of standard mirrors, as shown in the plate, is mounted, by means of sealing wax, in blackened wooden frames, 18 cm. long by about 7 cm. wide, and 4 to 5 mm. thick. The inner dimensions of the frames are 12 cm. by 4.5 cm. The bottom of the box carries a rabbet of tin, on which the frames may be slid, thus bringing the mirrors under the eyeholes. A second rabbet above the first allows the introduction of a frame carrying the mirror to be compared, which may thus be brought between any two of the standards and compared just as in nesslerisation. The box is mounted over a white paper or plate, in front of a good light. The calculation of the amount of arsenic in the area of paper taken follows from the determination of the amount in the aliquot part of the solution. From this can be found the number of milligrams per square meter, which, when multiplied by the factor, 0.0128, gives the number of grains per square yard.

Appendix.—Analytical and Experimental Work.

The experimental work in the investigation of the availability of the method is given in detail in the following pages.

1. *Necessity of Charring.*—Considerable difference of opinion exists as to the necessity for insuring the absence of organic matter in the extract to be tested. Odling,[1] in 1859, in testing for arsenic in tissues, found that he could obtain arsenic by Reinsch's test in the presence of organic matter, but not by Marsh's. After getting rid of the organic matter by distillation with hydrochloric acid, he had no difficulty with the Marsh test. Blondlot[2] calls attention to the necessity of completely destroying the organic matter. Chittenden and Donaldson,[2] on the other hand, were able, in the presence of organic matter, to detect very small amounts of arsenic, and consider it of no hindrance. My experience has been, that, while the organic matter may not completely prevent the deposition of small amounts, and is no hindrance in the detection of large amounts, yet the character of the mirror is so altered that comparison with the standards is impossible. Besides, the organic matter causes an increased and irregular flow of gas, which tends (App. 5. *f*) to carry undecomposed arseniuretted hydrogen out of the tube. I therefore take the precaution, by thoroughly charring, to insure the absence of organic matter in the extract.

[1] Guy's Hospital Reports, 5, 367-374. [2] Loc. cit.

Thoms[1] digests 100 sq. cm. of the paper on the water-bath with (1–7) sulphuric acid, and adds the filtrate directly to the reduction-flask. Fleck[2] considers that digestion with a 25-per cent. sulphuric acid is sufficient to extract the arsenic completely, and Reichardt[3] concurs in this opinion. I cannot agree with this, and consider that the chance of the arsenic being held as arsenious sulphide is alone enough to condemn the method (App. 2. *c*), not to speak of the organic matter extracted.

2. *Use of an Oxidising Agent in Charring.*—In case the paper contains chlorides, it seemed likely that a portion of the arsenic would be volatilised during the treatment with sulphuric acid. This was found to be true to an extent sufficient to warrant the precaution of adding a small quantity of nitric acid to the sulphuric acid, in order to prevent the formation of arsenious chloride.

a. The Presence of Chlorides in Wall Papers.—In order to determine to what extent chlorides exist in wall-papers, several analyses were made of papers taken at random. The method was as follows: A measured amount of paper (400 sq. cm.) was thoroughly moistened with a strong solution of potassic nitrate (free from chlorine) on a broad porcelain plate, dried on the plate, and ignited over the plate. The organic matter was practically destroyed. The residue was transferred from the plate to a chlorine-free filter, and washed thoroughly with hot water. The filtrate, after acidification with dilute sulphuric acid, was boiled to expel nitrous acid, and, after cooling, titrated according to Volhard with approximately hundredth-normal solutions. There is no danger of volatilisation of hydrochloric acid even on prolonged boiling, as Gooch and Mar[4] have shown that a solution containing 0.12 per cent. of hydrochloric acid can be boiled down one-half without appreciable loss. In titrating, as well as in determining the strength of the standard solutions, it was found that the dilution of the solution affected the end-reaction in that the color of the ferric sulpho-cyanate was obscured by that of the argentic chloride, even if the latter were made to "clump together." This difficulty was easily obviated by heating to boiling after adding excess of argentic nitrate, filtering off the chloride, and titrating back in the cooled filtrate. The end-reaction was then as sharp as possible.

Analysis of thirteen papers gave an average of 138 milligrams

[1] Loc. cit. [2] Rep. analyt. Chem. 1883, Heft 2. [3] Archiv d. Pharm. **221**, 271.
[4] Amer. Jour. Science [3] **39**, 293.

of chlorine per square meter, or 1.38 mgr. in the usual amount (100 sq. cm.) taken for the determination of arsenic. The highest amount was 238 mgr., the lowest 56 mgr. In no case was a paper found free from chlorides.

b. Effect of Chlorides.—A solution of sodic chloride free from arsenic was made up of such strength that 1 cc. contained 1 mgr. chlorine. Several trials were made of the effect of a known amount of chloride on small amounts of arsenic. 100 sq. cm. S. & S. filter-paper (589) were used in each case. After addition of the arsenic and sodic chloride solutions, the paper was dried in the evaporating dish, and the arsenic determined exactly as described, but without using nitric acid. The following table shows the results obtained. Analyses 1–6 were made with duplicate readings which agreed closely.

	Mgr. As_2O_3 taken.	Cc. NaCl, mgr. Cl, taken.	Mgr. As_2O_3 recovered.	Percentage As_2O_3 recovered.
1	10.0	20.0	5.22	52.2
2	10.0	20.0	4.96	49.6
3	5.0	4.4	3.61	72.2
4	0.5	2.0	0.44	88.0
5	0.1	2.0	0.87	87.0
6	0.05	2.0	0.02	40.0
7	0.01	2.0	0.005	50.0

Analyses 1 and 2 show that the presence of twice the theory of chlorine causes a large loss, with an amount of arsenic comparatively large. Analysis 3 shows a marked loss with less than the theory. Analyses 4 to 7 were made with more chlorine than the average found (1.38 mgr.), but less than the greatest amount (2.38 mgr.); the amounts are respectively 4, 20, 40, and 200 times the theory, and the conditions are more nearly those met with in practice than in analyses 1 to 3. It will readily be seen that the loss is sufficient to warrant the precaution of using an oxidising agent.

c. Loss by Retention of Arsenic in the Char as Arsenious Sulphide.—The presence of the sulphide in papers is not very common. Yet papers colored with ultramarine occur frequently, and the sulphuretted hydrogen set free from this by the sulphuric acid acts on the arsenic compound, and thus a large part of the arsenic remains in the char as the sulphide, insoluble in dilute sulphuric acid. The following analyses of a paper are sufficient to show the

danger of loss from this source. The paper had a light blue ground, and the odor of sulphuretted hydrogen was apparent on addition of sulphuric acid. 100 sq. cm. charred with sulphuric acid and a few drops of nitric acid gave an amount of arsenic corresponding to 5.9 mgr. per square meter. 100 sq. cm. charred with sulphuric acid alone gave 4.5 mgr. per square meter. The char was then extracted with ammonia, and the extract evaporated with sulphuric acid and a drop of nitric acid. This yielded 0.01 mgr., corresponding to 1 mgr. per square meter and bringing the total amount up to 5.5 mgr., which agrees with the first analysis.

d. The Deposition of Arsenic from a Solution of Arsenic Acid.—The question arises whether the conversion of the arsenious to arsenic acid by use of an oxidising agent would cause the arsenic to be held back. This was quickly determined by comparison of the standard mirrors with a set prepared from a solution of arsenic acid, of which 1 cc. contained 0.01 mgr. As_2O_3, as As_2O_5. The mirrors agreed sharply. This is at variance with the results of Headden and Sadler,[1] who found, in using the method of Chittenden and Donaldson, that it was necessary to subject the arsenic acid to preliminary reduction in order to obtain all the arsenic present. The reason for this is, probably, that a very small quantity of arsenic acid, such as would occur under the conditions of this method, is more quickly reduced by nascent hydrogen, while the comparatively large quantity used by Headden and Sadler would take more time. They do not show that prolonged treatment in the Marsh reduction-flask would not have eliminated this error.

e. The Use of Nitric Acid as an Oxidiser.—Nitric acid suggests itself at once as the most convenient oxidising agent. In this connection may be mentioned the method proposed by Blyth,[2] which consists in soaking the paper in potassic chlorate, drying, burning, and extracting with water. Hager[3] substitutes sodic nitrate for the potassic chlorate. Many destroy the organic matter by hydrochloric acid and potassic chlorate, as in the case of tissues. Lyttkens[4] uses sulphuric acid and potassic chlorate, and Lenz,[5] commenting on this, considers it the best means of treatment of the paper. The German law[6] of 1888 prescribes the treatment of fabrics with strong hydrochloric acid and distillation with ferrous

[1] This Journal **7**, 338; Ber. d. chem. Ges. **19**, 116. [2] Loc. cit. p. 532.
[3] Pharm. Centralhalle **13**, 145.
[4] Ref. Ztschr. analyt. Chem. **32**, 147, from Landw. Versuchsstat. **26**, 305.
[5] Ztschr. analyt. Chem. **32**, 147. [6] Ibid. **27**, 471.

chloride. None of these methods in the analysis of wall-papers and fabrics have any advantage over charring with the simple addition of nitric acid, and all require more time.

That all the arsenic may be recovered when nitric acid is used is shown by the following: 0.01 mgr. arsenious oxide was added to 100 sq. cm. of filter-paper and a drop of strong nitric acid added before charring. The mirror obtained corresponded to 0.01 mgr.

1 mgr. As_2O_5 and 5 cc. sodic chloride solution (5 mgr. chlorine) were added to 100 sq. cm. filter-paper and treated with a mixture of one part nitric to six parts sulphuric acid. Duplicate readings gave 1.095 mgr. recovered, an error no greater than that which might occur from the method.

10 mgr. As_2O_3, as As_2O_5, were added to 100 sq. cm. filter-paper, and treated with sulphuric acid alone. Duplicate readings gave 9.94 mgr. recovered.

Finally, 100 sq. cm. of a wall-paper containing no arsenic was, after addition of varying amounts of As_2O_3, charred with a nitro-sulphuric acid containing one part nitric to thirty of sulphuric acid. The following table shows the results of four analyses. The readings on 2, 3, and 4 were in duplicate.

	Mgr. As_2O_3 taken.	Mgr. As_2O_3 found.	Mgr. per Sq. Meter taken.	Mgr. per Sq. Meter found.
1	0.01	0.009	1.0	0.90
2	0.10	0.0995	10.0	9.95
3	1.00	0.977	100.0	97.70
4	10.00	10.30	1000.0	1030.00

f. Effect of Free Nitric Acid in the Reduction-flask.—Rieckher[1] does not consider the presence of free nitric acid to be detrimental, while Fresenius[2] takes the opposite ground. Blondlot[3] thinks that free nitric acid gives rise to the formation of a solid hydride of arsenic on the zinc, thus causing the retention of part of the arsenic. Without discussing the correctness of this statement, which seems to have been quite universally accepted, we have only to consider the effect of a trace of the acid on the deposition of the mirror, as the method of charring would leave, at most, but a very small amount of free nitric acid in the extract. 0.02 mgr. and 0.05 mgr. As_2O_3 were added to the reduction-flasks in which were about 20 cc. dilute sulphuric acid, and immediately

[1] Neues Jahrb. f. Pharm. **20**, 3. [2] Ztschr. analyt. Chem. **2**, 389.
[3] Comptes Rendus **57**, 596.

afterward a drop of strong nitric acid was added to each. The dilution was considerable, but not so great as might occur in practice. The mirrors were clearly defined, and corresponded sharply to 0.02 mgr. and 0.05 mgr. respectively.

3. *Extraction of the "Char."*—It is necessary that the char should be thoroughly pulverised and extracted with *hot* water. Considerable loss is likely to occur if these precautions are disregarded, as the following results show:

To 100 sq. cm. of a wall-paper free from arsenic, 1 mgr. As_2O_3 was added, and the char was extracted with 30 cc. cold water. 0.77 mgr. was recovered = 77 per cent.

To the same amount of paper 5 mgr. were added, and the char extracted with 30 cc. cold water. 3.82 mgr. were recovered = 76.4 per cent.

To the same amount of paper 10 mgr. were added, and the char extracted as before, but, in addition, the particles were well triturated. 9.19 mgr. were recovered = 91.9 per cent.

That this loss was not due to error in estimation of the mirrors was shown by repetition of the first two trials, mirrors being obtained from separate portions of the same extract. The char was triturated in each case:—

1 mgr. As_2O_3 gave 0.9 mgr. and 0.9 mgr. Average, 90 per cent.

5 mgr. As_2O_3 gave 2.92 mgr. and 2.95 mgr. Average, 58.60 per cent.

That arsenic would be left in the char was shown as follows: 100 sq. cm. of paper as above, after addition of 5 mgr. As_2O_3, were charred, and the finely ground mass extracted first with cold water. 3.11 mgr. were recovered = 62.2 per cent. The residue was then extracted with 30 cc. hot water. 1.63 mgr. were recovered = 32.6 per cent. A third extraction with hot water gave a solution free from arsenic. Total amount recovered = 4.74 mgr. = 94.8 per cent.

The quality of the paper has no effect on the loss: 5 mgr. As_2O_3 were added to 100 sq. cm. filter-paper and treated as before. Two readings from the same cold extract gave 3.51 and 3.46 mgr. respectively. Average, 69.9 per cent. Finally, to show the practical completeness of extraction with only 25 to 30 cc. hot water, 100 sq. cm. of filter-paper were charred with different amounts of arsenious oxide.

	Mgr. As_2O_3 taken.	Mgr. As_2O_3 recovered. Extract 1st.	2d.	3d.	Total.	Percentage As_2O_3 recovered.
1	5.0	4.99	0.08	0.0	5.07	101.4
2	5.0	4.98	0.07	0.0	5.05	101.0
3	10.1	10.65	0.06	0.0	10.71	106.7
4	10.0	10.37	0.0	...	10.37	103.7

10 mgr. of arsenious oxide per 100 sq. cm. of paper would correspond to 1000 mgr. per sq. meter, which is an unusual amount. Hence any smaller amounts would be easily extracted. It should be borne in mind that the error is necessarily great in such large amounts, for the deposit which is compared with the standards is so small a proportion of the total amount that a slight difference in reading is proportionally increased.

4. *Reagents.*—Many chemists prefer to use hydrochloric acid instead of sulphuric acid, on account of the quicker action of the former on the zinc. Opinions vary considerably as to the error arising from volatilisation of zincic chloride, and consequent deposition at the heating place, when hydrochloric acid is used. Liebig,[1] very soon after the publication of Marsh's method, called attention to possible error from this source, and several years later Wackenroder[2] confirmed Liebig's opinion. Beckurts[3] claims that there is no danger to be feared, but does not show conclusively that this is the case. Brescius[4] recognises the chance of error, and recommends passing the gas through sulphuric acid, if hydrochloric acid is used for generation. The committee of the British Health Association, above referred to, recommends the use of hydrochloric acid, without comment on its possible disadvantage.

While the volatilisation of zincic chloride might not interfere with the detection of arsenic in considerable quantity, yet it is of primary importance in this method for the mirror to be of arsenic alone, and hence capable of comparison with standards. We cannot, therefore, run the risk of the small mirror being contaminated by any impurity whatever. For this reason, if for no other, the use of hydrochloric acid is wholly unadvisable. Then the time gained in using hydrochloric acid is not to be considered in this method, as the use of a constant generator reduces the time of analysis so decidedly.

The same desire to hasten the evolution of hydrogen in the ordinary Marsh process has led to the addition of stimulants to

[1] Ann. Chem. (Liebig) **23**, 217.
[2] Archiv f. Pharm. **70**, 14.
[3] Ibid. **222**, 653.
[4] Dingl. Polyt. Jour. **186**, 226.

the action in the shape of platinic chloride or cupric sulphate. Bernstein[1] has shown that the use of platinic chloride is inadmissible, because arsenic is thereby held back. At the same time, however, he finds no loss when the zinc is platinised or silvered before being used. Headden and Sadler[2] agree with Bernstein in the case of platinic chloride, and find that cupric sulphate also causes a loss. They also get low results by using a spiral of platinum wire in contact with the zinc. Here, again, the use of the constant generator precludes the necessity for increasing the sensitiveness of the zinc.

Mohr,[3] in 1837, called attention to the fact that the residual zinc even after careful washing contained arsenic. This would seem to substantiate the statement of Blondlot, quoted above, concerning the solid hydride of arsenic. Fresenius[5] also considers that the effect of nitric acid is due to the formation of a hydride. When we consider the case of the mere detection of arsenic by the Marsh process, where all the arsenic is not necessarily reduced to arseniuretted hydrogen, it is quite possible that part is left in the zinc, especially if the extract be not free from nitric acid. But in this method, where all of a very small amount of arsenic is to be reduced, and the action is pushed as far as possible, the probability is that no arsenic is left in the zinc. I have often, after deposition of the mirror, pushed the action as far as the complete solution of the zinc, and have never observed any increase of the mirror at the close. It would seem hardly possible for the solid hydride to remain in that state in a reducing medium for such a length of time (compare also 2. *f*). A large amount of carbon in the zinc is apt to cause too rapid evolution, but I cannot confirm the statement of Headden and Sadler[2] that zinc containing carbon causes a loss of arsenic, and that the zinc must in consequence be free from carbon.

5. *General Precautions.—a. Means of drying the Hydrogen.*— The use of sulphuric acid is not allowable. I have found the statement of Dragendorff[4] to be true, that sulphuric acid absorbs arseniuretted hydrogen. This is assumed by Janowsky[5] to be due to decomposition into arsenic and hydrogen, but no proof is given. Dragendorff[4] quotes the suggestion of Otto,[6] that a small amount of fused potassic hydroxide be placed before the fused calcic

[1] Inaug. Dissertation, Rostock, 1870. [2] Loc. cit. [3] Ann. Chem. (Liebig) **33**, 217.
[4] Ermittelung von Giften, 2te Aufl. p. 336. [5] Ber. d. chem. Gesell. **6**, 216.
[6] Ausmittelung der Gifte.

chloride, in order to absorb any sulphuric acid which might be carried over, it being possible that the acid might act on the calcic chloride, giving hydrochloric acid, which might form arsenious chloride and thus cause loss of arsenic. The potassic hydroxide would also hold back sulphuretted hydrogen. It is well known that potassic hydroxide absorbs antimoniuretted hydrogen, and it has been recently shown by Kuhn and Saeger,[1] as well as by Headden and Sadler,[1] that arseniuretted hydrogen is also absorbed by it. There is, however, no need of its use as a precaution against either of the contingencies mentioned above.

Lyttkens[1] considers sulphuric acid to be a better drying agent than calcic chloride, and Lenz[1] agrees with him, but neither shows that there is no loss of arsenic attending its use.

As to Headden and Sadler's[1] statement, unsupported by analysis of the calcic chloride used, that fused calcic chloride holds back arsenic when moist, I have never met with any indication that there was danger of loss from this source.

b. Impurities in the Glass of the Deposition-tube.—The errors resulting from the presence of lead and arsenic in glass have been frequently mentioned. The presence of lead in any hard glass fit for use is scarcely probable. The formation of a mirror from either of these sources would, however, be detected at the start, and the glass rejected at once. I have not found any case of error attributable to impurities in the glass.

c. Temperature of the Reduction-flask.—Dragendorff[2] quotes Kolbe[3] as having shown that sulphuretted hydrogen is always formed by the action of sulphuric acid on zinc, if the reaction temperature exceeds 30°, and recommends on this account that the flask be cooled. The quotation is misleading. What Kolbe showed—and Fordos and Gélis[4] called attention to the same point some time before Kolbe—was, that if strong acid be added to the flask to increase the action, there was reduction of the acid at the temperature mentioned. With acid diluted with two parts of water no reduction took place. As one would hardly add strong acid to the flask, the danger of formation of sulphuretted hydrogen from mere action of the acid on the zinc is not to be feared. Yet it is necessary to keep the flask cool in some such manner as suggested, if only to prevent too violent action of the acid which may occur from accidental presence of organic matter.

[1] Loc. cit. [2] Loc. cit. p. 336. [3] Ann. Chem. (Liebig) **119**, 174.
[4] Comptes Rendus **13**, 437.

d. Necessity of boiling the Char with Water.—The formation of a "sulphur mirror" is often met with, due to the decomposition of sulphuretted hydrogen at the heating place. Then, too, Brunn[1] has lately shown that sulphuretted hydrogen and arseniuretted hydrogen form, when heated, hydrogen and arsenious sulphide. The necessity of boiling the char with water is therefore evident, in order that no sulphur dioxide be left in the extract to be reduced by the nascent hydrogen.

e. Beginning of Heating.—If the tube be heated as soon as the hydrogen is lighted, the small amount of oxygen left in the flask causes the formation of water in the deposition-tube. This can be avoided, if desired, by waiting a few minutes before setting the lamp under the tube.

f. Rapidity of Gas-flow and Amount of Heat.—In the method of Chittenden and Donaldson it is necessary to guard against too rapid evolution of gas, and the heating surface must be very great in order that no arseniuretted hydrogen shall escape decomposition. In this method, the amount of heating surface need not be greater than that given by a good burner, and I have assured myself by direct experiment that no arsenic escapes under the ordinary conditions when the size of the mirror is not above 0.06 mgr. It is necessary, however, for the stream of gas to be slow and regular. Hence the disadvantage of organic matter in the extract, causing an increased and irregular flow of gas.

6. The following table contains some analyses, taken at random, illustrative of the method:—

	Sq. Cm. taken.	Grams Extract.	Gr. Extract taken.	Mirror obtained Mgr. As_2O_3.	Mgr. As_2O_3 found.	Mgr. As_2O_3 found per Sq. Meter.
1	100	33.17	33.17	0.030	0.030	3.0
2	100	32.27	6.00	0.017	0.094	9.4
			5.81	0.015	0.083	8.3
3	100	31.84	5.66	0.045	0.253	25.3
			1.90	0.015	0.251	25.1
4	25	29.69	2.64	0.016	0.179	71.9
			2.65	0.017	0.191	76.2
5	111.15	33.66	0.78	0.035	1.510	136.0
			0.46	0.020	1.460	132.0
6	25	30.67	1.01	0.040	1.214	485.6
			2.08	0.080	1.180	472.0
7	12	28.83	0.48	0.030	1.802	1502.0
			0.61	0.043	2.032	1693.0

[1] Ber. d. chem. Ges. **23**, 3202.

7. *Comparison of Results obtained by the Berzelius-Marsh Process with those obtained by other Methods of Analysis.*—In order to test the availability of the process, it became necessary to analyse, by one of the general quantitative methods, some of the papers which had been analysed by the Berzelius-Marsh method. In the analyses given below, the eventual determination was made by an approximately hundredth-normal solution of iodine, and, when necessary, titrating back with a sodic thiosulphate solution of corresponding strength. I find a similar method to have been proposed some time ago by Holthof.[1] Considerable difficulty was met with at first in finding a suitable method of getting the arsenic from the paper into proper state for titration. A measured piece of paper (100–400 sq. cm.) was treated on a porcelain plate with a strong solution of potassic nitrate, dried on the plate, burned over the plate, and the residue washed off into an evaporating dish. The residue was then treated with about 5 cc. strong sulphuric acid and evaporated until sulphuric acid fumes appeared. To insure the complete expulsion of nitric and nitrous acids, the mass was boiled down again, after addition of a little water. It was then taken up with hot water, filtered, and washed with hot water. The filtrate was kept at 60°–70° for half an hour, and sulphur dioxide passed through. After boiling the reduced solution in the flask until sulphur dioxide was expelled, it was made alkaline with sodic bicarbonate, cooled and titrated. The results obtained were far from satisfactory, but the analyses agreed closely in three cases, which are given below. (Papers numbered 111, 395, and 42 in final table.)

Next, instead of ignition with potassic nitrate, the paper was treated exactly as in the Berzelius-Marsh method, with nitrosulphuric acid (1–30), taking care to get rid of all nitric and nitrous acids. The extract was reduced at 60°–70° by sulphur dioxide, the excess of the latter driven off by boiling, and the cooled solution made alkaline with sodic bicarbonate, and titrated. In one case the arsenic was precipitated from the extract by sulphuretted hydrogen, and the arsenious sulphide converted to arsenious acid, and titrated. The amount of time required for this, however, offset any advantage from it. Although by care this method can be employed, yet the details require much time and the chances for error are many. Duplicate analyses agreed closely in two

[1] Ztschr. analyt. Chem. **23**, 378.

cases, which are given below. (Papers numbered 194 and 155 in final table.)

The method finally used was adapted from the well known process of Schneider[1] and Fyfe.[2] A measured quantity of paper was cut into small pieces and placed in a 500 cc. distilling flask connected with a cooler. Attached to the latter was a receiver with a second tubulus carrying a long tube which served as an air cooler. About 100 cc. of hydrochloric acid, diluted one-half, were added to the flask, and the mixture distilled, slowly, almost to dryness. It was found by trial, that in nearly every case all the arsenic came over in one distillation, and, if not, that a mere trace was left in the residue. The distillate was transferred to a flask, potassic chlorate added, the solution boiled down one-half, transferred to an evaporating dish, and evaporated to dryness, with the addition of a few drops of strong sulphuric acid. The residue was generally white. If dark, from presence of volatile organic matter not destroyed by the potassic chlorate, the addition of a few drops of strong nitric acid and evaporation expelled the organic matter. The residue was then washed into a flask with about 50 cc. water, and reduced and titrated as in the previous cases.

The method was tested by the following analyses of filter-paper to which known amounts of arsenic were added, 200 sq. cm. of paper being used in each case.

	Mgr. As_2O_3 taken.	Cc. Iodine used. 1 cc.=0.9815 mgr. As_2O_3.	Mgr. As_2O_3 found.	Percentage As_2O_3 found.
1 *a*	5	5.1	5.01	102.1
1 *b*	5	5.3	5.20	
2 *a*	5	5.0	4.91	100.1
2 *b*	5	5.2	5.10	
3 *a*	25	25.1	24.64	98.4
3 *b*	25	25.0	24.54	

The residues from the distillations in the last analyses were, after the addition of a few drops of nitric acid, charred with sulphuric acid and "marshed," giving mirrors corresponding to 0.015 mgr. and 0.02 mgr. respectively, showing that a mere trace was left in the flasks.

The following papers were analysed by this method:—

[1] Jsb. Chem. 1851, p. 630. [2] J. prakt. Chem. **55**, 103.

Number of Paper.	Sq. Cm. taken.	Cc. Iodine used. 1 cc. = 0.9815 mgr. As_2O_3.	Mgr. As_2O_3 found per Sq. Meter.
194	200	17.20	844.00
194	200	17.30	849.00
406	400	3.10	76.07
406	400	3.00	73.61
39	400	2.80	68.71
39	400	2.70	66.25
392	380	1.80	46.50
393	400	0.38	9.33
393	400	0.36	8.83
359	400	1.30	31.90
359	400	1.10	27.00

Finally, the following table shows the comparison of the results obtained by the volumetric method with those obtained on the same papers by the Berzelius-Marsh method. The first two columns compare the results in milligrams per square meter, and the second two in grains per square yard. Each result is the mean of two, unless specified.

Number of Paper.	Mgr. As_2O_3 per Sq. Meter.		Grains per Sq. Yard.	
	Berz.-Marsh.	Volumetric.	Berz.-Marsh.	Volumetric.
393	8.8	9.1	0.11	0.12
359	24.0	29.5	0.31	0.38
392	46.8	46.5 [1]	0.60	0.60 [1]
39	64.9	67.5	0.83	0.86
406	72.8	74.9	0.94	0.96
111	110.4	108.7	1.42	1.39
395 [2]	193.0	210.4	2.47	2.69
42	478.8	421.8	6.13	5.40
194	842.0	832.7 [3]	10.78	10.66 [3]
155	1527.1	1478.5	19.55	18.93

Before the above described method was worked out, it was thought that it would give merely an approximation of the amount of arsenic in wall-papers and fabrics, which would allow one, for instance, to pass judgment on the articles from a sanitary standpoint. Not only, as will be seen from the table, does the method give an approximation to the actual amount when ordinarily conducted, but with care it can be made to give results worthy of

[1] One determination.

[2] 395 was a piece of "Turkey red" cloth.

[3] Four determinations.

comparison with other quantitative methods. The greatest error occurs naturally in the estimation of large amounts, but in this case an approximation would answer until a more exact determination was called for.

The process will, I think, be also found of great value in toxicological work, not only as a rapid means of determining the quantity of arsenic present, and as a check on other methods, but also as the only means of accurately determining the amount when the arsenic is present in minute quantity. In such work the organic matter would not generally be charred, but the arsenic would be extracted by the method of distillation. I hope to investigate the extension of the method to toxicological work.

The limit of arsenic that I have been able to detect with certainty by the Berzelius-Marsh method is 0.001 mgr. As_2O_3 or 0.0007 mgr. As. I shall not here take up the much discussed question of the delicacy of this as compared with other methods, but I think it will be agreed that no other method enables one to determine quantitatively such small amounts.

In conclusion, I have to thank my assistant, Mr. Charles Walker, very sincerely for his valuable services in most of the analytical work of this paper.

UNITED STATES NAVAL ACADEMY, ANNAPOLIS, MD.,
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Contributions from the Sheffield Biological Laboratory of Yale University.

A STUDY OF THE PROTEIDS OF THE CORN OR MAIZE KERNEL.

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The character of the proteids present in the kernel or seed of corn or maize, the most important of American cereals, has up to the present time never been investigated to any great extent. In fact, our knowledge of this subject has been practically limited to the observations of Ritthausen[1] concerning "maize fibrin," a body

[1] Die Eiweisskörper der Getreidearten, Hülsenfrüchte und Ölsamen, Bonn, 1872, p. 113.

soluble in alcohol, and to the bare statement made by Th. Weyl[1] that the powdered seeds of maize yield to a 10-per cent. solution of sodium chloride a globulin-like substance which, after purification by repeated precipitation with water and re-solution in salt water (10 per cent.), coagulates at 75° C. It is a fair presumption, however, judging from the interesting results obtained by Sidney Martin, Vines and other workers among the vegetable proteids, that the proteids of the corn kernel must doubtless be as numerous and complex as those of other seeds already investigated, and this we have indeed found to be the case. In fact, the subject, while more or less fruitful in results, has proved an exceedingly complex one, on account of the large number of different proteids present in the seed, the small quantities present, and the ease with which several of the bodies, especially the globulins, are apparently converted into other forms. Again, in view of the probable widespread distribution of the vegetable proteolytic ferments, any study of the vegetable proteids normally present in seed or fruit must necessarily be complicated by possible ferment changes, through which new bodies may be formed.

Our study of the subject has naturally divided itself into three main parts: 1st, a study of the proteids soluble in salt solutions, but insoluble in water; 2d, a study of the proteids soluble both in water and in dilute salt solutions; 3d, a study of the proteid matter soluble in alcohol, but insoluble in water and salt solutions.

I. Proteids Soluble in Salt Solutions, but Insoluble in Water.

Finely ground corn meal[2] extracted with a 10-per cent. solution of sodium chloride yields a slightly opalescent fluid, moderately rich in globulin-like bodies. A simple aqueous extract of ground corn likewise contains more or less globulin held in solution by the salts dissolved from the corn. From both solutions the globulins are slowly precipitated by dialysis of the salts, and partially so by addition of water. They are, moreover, completely precipitated, mixed with other proteids, on saturation of their solutions with ammonium sulphate.

a. *Direct extraction of corn meal with 10-per cent. solution of sodium chloride, and separation of the globulin by dialysis.*

[1] Ztschr. für physiolog. Chem. **1**, 84.

[2] All the corn used in these experiments was of one variety, known as White Dent, and was freshly ground to a fine powder prior to each experiment.

In view of the well known action of water, in the presence of possible ferments, on the globulins of some seeds, the first extractions of the corn kernel were made with salt solutions, with a view to diminishing the possibility of cleavage or dissociation of the normal proteids of the kernel. 5 kilos. of finely ground corn meal were therefore soaked in 8 litres of 10-per cent. solution of sodium chloride, with frequent stirring, for 24 hours, after which the fluid was strained off and the residue placed in a screw-press and squeezed dry. A second extraction of the meal was made with 4 litres of fresh salt solution, and the two extracts united. The solution was then filtered through thick filter-paper, yielding an almost perfectly clear yellowish filtrate.

Tested by fractional heat-coagulation a series of coagulums were obtained commencing at about 35°–40°, a final one making its appearance as the solution was boiled. Further, the clear filtrate from this precipitate gave on addition of acetic acid a flocculent precipitate of proteid matter, all of which may be taken as evidence of the presence of a variety of proteid bodies, coagulable and non-coagulable by heat.

The entire salt solution, with its content of proteids and other substances, was then dialysed[1] in a stream of running water for a period of six days, at the end of which time chlorides were entirely removed. As the percentage of salt in the solution began to diminish a heavy white precipitate made its appearance, which steadily increased in amount as the removal of the salt was continued, leaving a perfectly clear fluid containing some coagulable proteids. The globulin precipitated in this manner was separated from the fluid by decantation, washed somewhat with distilled water, and then redissolved in a 10-per cent. solution of sodium chloride. This latter solution was somewhat turbid even after repeated filtration. A portion tested by heat-coagulation gave the following results: At 60° the fluid became decidedly turbid, with formation of flocks at 64°. The temperature was then raised to 68° and the mixture filtered. The clear filtrate became turbid at 74°, with formation of a flocculent precipitate at 79°, which was filtered off when the temperature reached 82°. The filtrate from this precipitate became turbid at 83°, with separation of flocks at 87°. The temperature was then raised to 90° and the precipi-

[1] During these long periods of dialysis, putrefactive changes were prevented by the occasional addition of a few drops of a 20-per cent. alcoholic solution of thymol.

tate filtered off. This filtrate on being heated to boiling gave no precipitate at first, but as the boiling was continued considerable flocculent matter gradually made its appearance. The largest coagulum was obtained at 79°. If we are to trust the results of this fractional heat-coagulation, the natural inference would be that the globulin-like substance separated by dialysis from the sodium-chloride extract of the corn meal is made up of several distinct globulins, or else that the one globulin possibly present is broken apart into several fragments by the action of heat.

The main portion of this sodium-chloride solution of the globulin was dialysed until the salt was entirely removed, a process which took five days and which left the globulin completely precipitated on the sides of the parchment. The peculiar, somewhat granular, appearance of the deposit led us to examine it under the microscope, when it was seen to be composed entirely of spheroids, thus showing a close approach to crystallisation. The precipitate was collected on a filter, washed with water, alcohol and ether, and when air-dried was found to weigh 10.1 grams, thus indicating about 0.2 per cent. of globulin in the air-dry kernel, on the assumption that the extraction and separation were complete. The filtrate from this last separation of the globulin was almost entirely free from proteid matter, giving only a very slight reaction with Millon's reagent, no further separation of any matter by continued dialysis, neither any precipitate on addition of acetic acid or acetic acid and solution of salt, and only the faintest turbidity on boiling.

A portion of the globulin dissolved in 10-per cent. solution of salt yielded by heat-coagulation much the same results as the previous salt solution of the proteid, viz. turbidity at 58°, formation of flocks at 67°. In the filtrate from this coagulum a second turbidity appeared at 77°, followed by flocks at 87°. Further, in this filtrate another coagulum appeared on boiling the solution, so that while the individual temperatures of coagulation were somewhat different from the preceding, they point to essentially the same general conclusion.

A portion of the globulin was dried at 110° C. until of constant weight, and then analysed with the following results:

Analysis[1] *of Corn Globulin, Preparation A.*

I. 0.3933 gram substance gave 0.2325 gram $H_2O = 6.57$ per cent. H, and 0.7250 gram $CO_2 = 50.42$ per cent. C.

II. 0.3693 gram substance gave 0.2182 gram $H_2O = 6.55$ per cent. H, and 0.6845 gram $CO_2 = 50.55$ per cent. C.

III. 0.3038 gram substance gave 44.1 cc. N at 10° C. and 761.4 mm. pressure = 17.62 per cent. N.

IV. 0.3067 gram substance gave 44.1 cc. N at 8.5° C. and 757.8 mm. pressure = 17.47 per cent. N.

V. 0.5111 gram substance fused with $KOH + KNO_3$ gave 0.0406 gram $BaSO_4 = 1.08$ per cent. S.

VI. 0.6773 gram substance fused with $KOH + KNO_3$ gave 0.0440 gram $BaSO_4 = 0.89$ per cent. S.

VII. 0.5265 gram substance gave 0.0102 gram ash = 1.93 per cent.

Percentage Composition of the Ash-free Substance.

							Average.
C	51.41	51.54	..	..	..	..	51.48
H	6.69	6.67	..	..	..	..	6.68
N	..	..	17.97	17.82	..	..	17.90
S	..	..	..	..	1.10	0.91	1.01
O	..	..	..	..	..	..	22.93
							100.00

b. *Direct extraction of corn meal with 10-per cent. solution of sodium chloride, and separation of the globulin by ammonium sulphate and dialysis.*

25 kilos. of corn meal were extracted with 50 litres of 10-per cent. salt solution, and the residue of meal extracted a second time with 16 litres of salt solution. The two extracts were united, filtered through paper, and the clear fluid saturated with pure ammonium sulphate. This gave rise to a more or less sticky precipitate composed of all the proteids present in the extract. The precipitate so obtained was filtered off, dissolved in water as far as possible, and then treated with 10-per cent. salt solution. The portion remaining insoluble was washed with salt solution as long as anything was removed, and then reserved for further treatment.

The solutions of the ammonium-sulphate precipitate in water (or rather in dilute ammonium sulphate) and in 10-per cent. sodium

[1] Carbon and hydrogen were determined by combustion in a current of oxygen, in an open tube, the vapors passing over a fairly long layer of coarsely granulated oxide of copper, a shorter layer of chromate of lead, and an anterior roll of freshly reduced metallic copper. Nitrogen was determined by combustion with oxide of copper after the Dumas method, while sulphur was estimated by Hammarsten's modification of Liebig's method.

chloride were united and dialysed for two weeks, at the end of which time a large amount of globulin had separated from the solution. The clear fluid, however, still contained some globulin, and was therefore reserved for further examination. The separated globulin was filtered off and redissolved in about 2 litres of 10-per cent. solution of sodium chloride, leaving almost no insoluble residue, and the solution again dialysed until the globulin had separated. This required seven days. The product, after being washed and air-dried, weighed 42 grams, and was composed wholly of spheroids. The filtrate from this latter deposit of globulin was again returned to the dialyser, but failed to give any further separation of globulin even after ten days' continued dialysis.

It is to be observed here that the separation of this globulin from a pure sodium-chloride solution is fairly rapid and quite complete, whereas the presence of ammonium sulphate interferes decidedly with its precipitation by dialysis, doubtless on account of the slower rate of diffusion characteristic of this salt.

The globulin prepared in this manner was readily soluble in salt solution, leaving only a slight insoluble residue. Subjected to heat-coagulation, the following results were obtained with a moderately large amount of globulin in a 10-per cent. solution of sodium chloride: The solution became turbid at 62°, with separation of flocks at 76.5°. The mixture was then kept at 78° for half an hour, after which it was filtered, the filtrate yielding a further turbidity at 83°, with separation of flocks at 93°. This latter coagulation was considerably heavier than the one at 76°. On boiling the solution, there was a slight increase in the amount of coagulum, which was still further increased by the addition of a drop or two of very dilute acid. Hence, this product shows approximately the same general range of heat-coagulation points as the preceding preparation, separated by simple dialysis from the original sodium-chloride extract. As the salt solution of the globulin showed a faint alkaline reaction, another test was made with a solution of approximately the same strength as the preceding, but carefully neutralised. This solution grew turbid at 64°, with formation of flocks at 76.5°. The mixture was filtered at 77°, and on being heated further became turbid at 82.5°, with separation of flocks at 91°. The filtrate from this latter precipitate became turbid on boiling, and yielded a large precipitate on addi-

tion of acetic acid. It is thus evident that the proteid dissolved in a neutral salt solution cannot be wholly coagulated by heat, even though the heating be continued for some time. In fact, the solution may be evaporated to dryness on a water-bath, the residue taken up again in water, and in the salt solution which results considerable proteid matter will be found dissolved and non-coagulable on further application of heat. In fact, the great bulk of this product appears to be non-coagulable by heat alone. Variations in the proportion of globulin dissolved in the 10-per cent. salt solution modify the temperatures of coagulation only slightly.

A portion of the substance dried at 110° C. until of constant weight was analysed with the following results, which, aside from a slightly higher percentage of carbon, show a close agreement in composition with the corresponding globulin A.

Analysis of Corn Globulin, Preparation B.

I. 0.3500 gram substance gave 0.2180 gram H_2O = 6.82 per cent. H.

II. 0.3251 gram substance gave 0.1992 gram H_2O = 6.81 per cent. H, and 0.6145 gram CO_2 = 51.55 per cent. C.

III. 0.3717 gram substance gave 0.7021 gram CO_2 = 51.52 per cent. C.

IV. 0.3592 gram substance gave 50.5 cc. N at 2.5° C. and 769.1 mm. pressure = 17.73 per cent. N.

V. 0.7523 gram substance fused with $KOH + KNO_3$ gave 0.0472 gram $BaSO_4$ = 0.86 per cent. S.

VI. 0.7871 gram substance fused with $KOH + KNO_3$ gave 0.0491 gram $BaSO_4$ = 0.85 per cent. S.

VII. 0.4622 gram substance gave 0.0025 gram ash = 0.54 per cent.

Percentage Composition of Ash-free Substance.

							Average.
C	..	51.83	51.80	..	..	..	51.82
H	6.85	6.84	..	..	..	..	6.85
N	..	..	..	17.82	..	..	17.82
S	..	..	..	..	0.86	0.85	0.86
O	..	..	..	..	..	..	22.65
							100.00

Another sample of globulin was prepared as follows: 2.5 kilos. of ground corn were extracted with about 10 litres of 10-per cent. solution of sodium chloride, and the extract, together with the washings, after filtration, saturated with ammonium sulphate. The precipitate was dissolved as far as possible in water and in 10-

per cent. salt solution, and the united filtrates dialysed until free from chlorides. The deposit of globulin, which gradually formed, was filtered off, washed with alcohol and ether, and dried at 110° C. until of constant weight.

On analysis it gave the following results:

Analysis of Corn Globulin, Preparation C.

I. 0.2307 gram substance gave 0.1442 gram H_2O = 6.95 per cent. H, and 0.4330 gram CO_2 = 51.17 per cent. C.

II. 0.3528 gram substance gave 51.5 cc. N at 11.5° C. and 745.6 mm. pressure = 17.26 per cent. N.

III. 0.3000 gram substance gave 0.0028 gram ash = 0.93 per cent.

Percentage Composition of the Ash-free Substance.

			Average.
C	51.64	..	51.64
H	7.01	..	7.01
N	..	17.42	17.42
S, O	..	..	23.93
			100.00

Still another preparation of globulin was separated in the following manner: 2.5 kilos. of corn meal were extracted with 12 litres of 5-per cent. solution of ammonium chloride, the residue of meal re-extracted with more ammonium-chloride solution, and the united filtrates precipitated with ammonium sulphate. This precipitate was dissolved as far as possible in water and 5-per cent. ammonium-chloride solution, leaving only a small insoluble residue, and the united fluids dialysed in running water for seven days. The globulin which separated was then dissolved in 10-per cent. solution of sodium chloride and redialysed until the salt was entirely removed. The precipitated globulin was then washed with water, alcohol and ether, and after being dried at 110° C. was analysed with the following results:

Analysis of Corn Globulin, Preparation D.

I. 0.1289 gram substance gave 0.0781 gram H_2O = 6.74 per cent. H, and 0.2432 gram CO_2 = 51.43 per cent. C.

II. 0.2639 gram substance gave 39.1 cc. N at 11° C. and 746.5 mm. pressure = 17.57 per cent. N.

III. 0.2561 gram substance gave 0.0012 gram ash = 0.47 per cent.

Percentage Composition of the Ash-free Substance.

			Average.
C	51.67	..	51.67
H	6.77	..	6.77
N	..	17.65	17.65
S	..	..	} 23.91
O	..	..	
			100.00

In these four preparations we have a good illustration of the general character of the globulin obtainable from the corn or maize kernel by direct extraction with salt solution. The product appears to be the same whether directly separated from its saline solution by dialysis, or first precipitated by ammonium sulphate and then separated by dialysis. The chemical composition of the four preparations is essentially identical, as seen from the accompanying table:

	Globulin A.	Globulin B.	Globulin C.	Globulin D.	Average.
C	51.48	51.82	51.64	51.67	51.65
H	6.68	6.85	7.01	6.77	6.82
N	17.90	17.82	17.42	17.65	17.69
S	1.01	0.86 } 23.93	23.93	23.91	0.93
O	22.93	22.65 }			22.91
	100.00	100.00	100.00	100.00	100.00

Many things, however, point to the view that the corn globulin separated from the kernel by the above methods is not a single substance, although we must continually keep in mind the possibility of unknown methods of cleavage which may perchance be facilitated by the very processes made use of in testing the globulin. Foremost among these is the peculiar and more or less variable range of coagulation-points obtained whenever a sodium-chloride solution of the globulin is subjected to fractional heat-coagulation. From the data thus obtained we might argue a variable mixture of phyto-myosin, vitellin, and some non-coagulable globulin. As to myosin, however, saturation of a salt solution of the globulin with salt crystals gives only a small precipitate, indicating but little of this substance. The next point suggestive of mixture is the fact that a portion of the globulin readily undergoes change into an insoluble modification by contact with water or strong salt solutions, while another portion is apparently very resistant to such action. Thus, in the precipitation of the globulin

by saturation with ammonium sulphate or by dialysis, more or less insoluble matter is formed (insoluble in 10-per cent. salt solution), but this amount grows less and less as the process is repeated, being apparently co-extensive with the amount of this changeable globulin present. The bulk of the globulin, however, retains its solubility in salt solutions by this treatment, under ordinary circumstances.

c. *Fractional separation of the above corn globulin by various methods.*

Treatment of the purified globulin with 10-per cent. salt solution, as stated above, almost invariably shows the presence of at least a small amount of substance insoluble in salt solution, possibly due to a partial conversion of the globulin into an albuminate by the action of water. It was further found that addition of water to a 10-per cent. salt solution of the globulin was followed by only a partial precipitation of the proteid. Hence an attempt was made to separate the globulin into three fractions for analysis. Accordingly, 5–6 grams of the air-dry globulin, Preparation A, were treated with about 300 cc. of a 10-per cent. solution of sodium chloride, and the insoluble matter collected on a filter and washed thoroughly with 10-per cent. salt solution. This residue was finally washed with water until the salt was entirely removed, then with alcohol and ether. It weighed 0.57 gram (Preparation A^1).

The salt solution and washings containing the bulk of the globulin, amounting to 430 cc., were diluted with distilled water to 4300 cc., by which an abundant precipitate was obtained. This was allowed to settle, then collected on a filter, washed free from chlorides, and lastly with alcohol and ether. It weighed 1.87 grams (Preparation A^2).

The dilute salt solution containing the remainder of the globulin, representing the more soluble portion, was dialysed in running water until the salt was entirely removed, at the end of which time the globulin had separated wholly in the form of *spheroids*. It was collected on a filter, washed with water, alcohol and ether, and weighed 1.6 grams (Preparation A^3).

These three fractions were dried at 110° C. until of constant weight, and analysed with the following results:

Analysis of Preparation A^2.

I. 0.5068 gram substance gave 0.3082 gram $H_2O = 6.75$ per cent. H, and 0.9540 gram $CO_2 = 51.34$ per cent. C.

II. 0.3622 gram substance gave 53.5 cc. N at 8° C. and 759.6 mm. pressure = 18.01 per cent. N.

III. 0.2994 gram substance gave 0.0025 gram ash = 0.83 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	51.76	..		51.76
H	6.80	..		6.80
N	..	18.16		18.16
S	..	..	}	23.28
O	..	..		
				100.00

Analysis of Preparation A³.

I. 0.2220 gram substance gave 0.1382 gram H_2O = 6.91 per cent. H, and 0.4132 gram CO_2 = 50.76 per cent. C.

II. 0.3221 gram substance gave 47.5 cc. N at 6° C. and 762.6 mm. pressure = 18.19 per cent. N.

III. 0.3318 gram substance gave 49.3 cc. N at 5.8° C. and 754.2 mm. pressure = 18.14 per cent. N.

IV. 0.2977 gram substance gave 0.0022 gram ash = 0.74 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	51.13	..	..	51.13
H	6.96	..	..	6.96
N	..	18.32	18.27	18.30
S	..	..	..	} 23.61
O	..	..	..	
				100.00

Analysis of Preparation A¹.

I. 0.3030 gram substance gave 36.5 cc. N at 5.8° C. and 758.8 mm. pressure = 14.79 per cent. N.

II. 0.1914 gram substance gave 0.0112 gram ash = 5.85 per cent.

Percentage of nitrogen in the ash-free substance = 15.59.

The following table shows the relationship of the several products:

	The original globulin. A.	Portion soluble in the dilute NaCl. A^3.	Portion insoluble in the dilute NaCl. A^2.	Portion insol. in 10-per ct. NaCl. A^1.
C	51.48	51.13	51.76	..
H	6.68	6.96	6.80	..
N	17.90	18.30	18.16	15.59
S }	1.01	23.61	23.28	..
O }	22.93			
Ash	1.93	0.74	0.83	5.85

From this it is to be seen that while there is no very radical point of difference in composition between the first three products, there are changes in the relative percentages which are strongly suggestive of admixture. Certainly that portion of the original globulin insoluble in 10-per cent. salt solution has a noticeably low percentage of nitrogen, surely low enough to account for the slightly higher percentages of nitrogen in the products A^3 and A^2. From the data here offered there is no positive evidence as to whether A^1 is an alteration-product of the original globulin, or whether it simply represents a small impurity. The former view is certainly the more plausible one, however, especially when it is remembered that this globulin had been dissolved in a salt solution and filtered two or three times previously. Again, it is to be noticed in comparing the two soluble products A^2 and A^3, that the body containing the lower percentage of nitrogen contains the higher percentage of carbon; and further, that in both products the percentage of nitrogen is by this treatment raised so as to correspond closely with the nitrogen content of pure phytovitellin.

In view of these results a portion of corn globulin was next separated into a number of fractions by the solvent action of various strengths of salt solution, and the several fractions studied, especially with reference to their composition and heat-coagulation points.

The globulin (Preparation E) was made from 5 kilos. of freshly ground corn by direct extraction with an abundance of 10-per cent. solution of sodium chloride, the proteids precipitated by saturation of the filtered solution with ammonium sulphate, this precipitate dissolved in water and salt solution, and the filtered fluid dialysed in running water for one week until the globulin had separated.

The entire quantity of globulin, about 10 grams, was then treated directly with one litre of 0.25-per cent. solution of sodium chloride at the temperature of the room and kept in agitation for about 3 hours. The residue was then filtered off and extracted again with one litre of salt solution of the same strength, the solution being kept in contact with the globulin for about 18 hours. This was likewise filtered off and the residue again extracted with two litres of 0.25-per cent. salt solution. A portion of the combined extract obtained in this manner, on being heated, grew

slightly turbid at 54°; this turbidity was still slight at 63°, but at 71° a flocculent coagulum appeared. No further coagulum appeared until the solution was boiled, and then only a slight one. The filtrate from this precipitate gave a faint reaction with acetic acid and potassium ferrocyanide. These united extracts were then placed in dialysers and dialysed in running water until the salt was entirely removed, when the deposited globulin was filtered off, and washed with alcohol and ether. It weighed air-dry 0.18 gram (Preparation E^1).

That portion of the globulin insoluble in 0.25-per cent. salt solution was placed in two litres of 0.5-per cent. solution of sodium chloride, and kept in contact with it for 18 hours or longer at 20° C., after which it was filtered off and treated with a fresh portion of salt solution of the same strength. The extract so obtained became turbid at 56°, and gave a flocculent coagulum at 75°. The filtrate from this coagulum became slightly turbid on boiling and gave a slight precipitate with acetic acid and potassium ferrocyanide. On dialysis of the 0.5-per cent. salt solution 0.527 gram of air-dry globulin was obtained (Preparation E^2).

The remainder of the globulin was next treated with 0.75-per cent. salt solution at 20° C. until all soluble matter was removed. A portion of the solution so obtained, on being heated, became turbid at 59°, with separation of flocks at 72.5°. The filtrate from this coagulum became turbid again at 79° and flocked at 85°. On boiling this filtrate a little more precipitate appeared. By dialysis of the united filtrates 2.32 grams of globulin were obtained (Preparation E^3).

The globulin still undissolved was then treated, after the manner described, with 1.0-per cent. salt solution as long as anything dissolved. This extract coagulated as follows: it became faintly turbid at 63°, with separation of flocks at 79.5°. The filtrate gave a second turbidity at 85°–87°, which increased slightly on boiling. By dialysis, 2.9 grams of globulin were obtained (Preparation E^4).

The residue of the original globulin was next treated with two litres of 2.0-per cent. salt solution, in which it nearly all dissolved. The slight residue was rejected. The extract coagulated as follows: turbid at 79°, with formation of flocks at 90°. The filtrate grew turbid again at 94°, with separation of flocks at 99°. On dialysis of the solution 2.2 grams of globulin were deposited (Preparation E^5). This substance, on being tested anew with 1.0-per cent. salt solution, was found practically insoluble.

The several products enumerated were dried at 110° C. until of constant weight, and then analysed with the following results:

Analysis of that Portion of the Globulin Soluble in 0.25-per cent. Solution of Sodium Chloride (E^1).

I. 0.1594 gram substance gave 21.6 cc. N at 4.0° C. and 772.3 mm. pressure = 17.04 per cent. N.

Not enough substance for an ash determination.

Analysis of that Portion of the Globulin Soluble in 0.5-per cent. Solution of Sodium Chloride (E^2).

I. 0.2470 gram substance gave 34.9 cc. N at 3.0° C. and 763.3 mm. pressure = 17.63 per cent. N.

II. 0.2170 gram substance gave 0.0075 gram ash = 0.69 per cent. ash.

Percentage of nitrogen in the ash-free substance = 17.74.

Analysis of that Portion of the Globulin Soluble in 0.75-per cent. Solution of Sodium Chloride (E^3).

I. 0.3303 gram substance gave 0.2018 gram H_2O = 6.79 per cent. H, and 0.6300 gram CO_2 = 52.02 per cent. C.

II. 0.3222 gram substance gave 0.1987 gram H_2O = 6.86 per cent. H, and 0.6125 gram CO_2 = 51.84 per cent. C.

III. 0.4261 gram substance gave 61.5 cc. N at 4.2° C. and 750.2 mm. pressure = 17.62 per cent. N.

IV. 0.3042 gram substance gave 42.9 cc. N at 3.0° C. and 764.1 mm. pressure = 17.61 per cent. N.

V. 0.4353 gram substance gave 0.0023 gram ash = 0.53 per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	52.25	52.07	..	..	52.16
H	6.82	6.89	..	..	6.86
N	..	..	17.69	17.68	17.69
S	..	..	..	..	23.29
O	..	..	..	..	
					100.00

Analysis of that Portion of the Globulin Soluble in 1.0-per cent. Solution of Sodium Chloride (E^4).

I. 0.3057 gram substance gave 0.1900 gram H_2O = 6.90 per cent. H, and 0.5814 gram CO_2 = 51.87 per cent C.

II. 0.5543 gram substance gave 76.0 cc. N at 3.3° C. and 774.2 mm. pressure = 17.33 per cent. N.

III. 0.3593 gram substance gave 50.0 cc. N at 3.0° C. and 754.3 mm. pressure = 17.16 per cent. N.

IV. 0.4353 gram substance gave 0.0023 gram ash = 0.53 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	52.14	..	..	52.14
H	6.93	..	..	6.93
N	..	17.43	17.26	17.35
S	..	..	..	} 23.58
O	..	..	..	
				100.00

Analysis of that Portion of the Globulin Soluble in 2.0-per cent. Solution of Sodium Chloride (E^5).

I. 0.3705 gram substance gave 0.2263 gram $H_2O = 6.79$ per cent. H, and 0.6995 gram $CO_2 = 51.50$ per cent. C.

II. 0.3632 gram substance gave 0.2209 gram $H_2O = 6.76$ per cent. H, and 0.6850 gram $CO_2 = 51.46$ per cent. C.

III. 0.4940 gram substance gave 70.3 cc. N at 3.0° C. and 755.4 mm. pressure = 17.57 per cent. N.

IV. 0.3434 gram substance gave 0.0028 gram ash = 0.81 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	51.92	51.88	..	51.90
H	6.84	6.81	..	6.83
N	..	..	17.71	17.71
S	..	..	..	} 23.56
O	..	..	..	
				100.00

The first thing to be noticed from these results is that only a comparatively small amount of the original globulin is soluble in very weak salt solutions. It is not until the solution contains 0.75 per cent. of salt that much globulin is dissolved. It is further noticeable that the weaker salt solutions have throughout a lower coagulation-point than the stronger salt solutions, and, moreover, that no one of the extracts coagulates completely at a given temperature, but shows some evidence, by a turbidity at least, of several different heat-coagulation points. As regards composition, the nitrogen of the several fractions is practically the same, and as this is apt to be the most variable element in proteid bodies, it is probable that the several fractions have essentially the same composition. It is further noticeable that the composition of the fractions E^3, E^4 and E^5 is practically identical with the composition of the globulins A and B, although the average content of carbon

in the former products is a trifle higher. Of the 10 grams of air-dry globulin started with, in this experiment, 8.12 grams were recovered in the several fractions. There was obviously some loss, especially in the many filtrations, so that this deficiency is not to be considered as representing the amount of globulin or alteration product insoluble in the 2.0-per cent. salt solution. The actual amount of insoluble matter was certainly far smaller than this.

It would have been interesting to have determined the percentage of nitrogen in the insoluble portion, but the quantity was so small and it was so mixed with shreds of filter-paper that the result in this case could have had little value.

The relationship of these several fractions or portions of the original globulin is clearly shown in the following table:

Portion soluble in NaCl	0.25 per ct.	0.50 per ct.	0.75 per ct.	1.0 per ct.	2.0 per ct.
C	..	..	52.16	52.14	51.90
H	..	..	6.86	6.93	6.83
N	17.04	17.74	17.69	17.35	17.71
S } O }	..	..	23.29	23.58	23.56
Coagulation-points,[1] 1st.	54°, 71°	56°, 75°	59°, 72.5°	63°, 79.5°	79°, 90°
" " 2d.	..	..	79°, 85°	85°, 87°	94°, 99°

This experiment, then, so far as it goes, corroborates the idea that the original globulin is a mixture of closely allied bodies possessed of different heat-coagulation points and of different degrees of solubility in dilute salt solutions. This method of treatment, however, is insufficient to bring about a complete separation of the individual bodies, the separate fractions obtained above being evidently themselves more or less mixtures, as indicated by their heat-coagulation points and their resemblance in chemical composition. This might indeed be possible, even if there were only two globulins present, for, as is well known, it is often as difficult to bring about a sharp separation of certain proteid bodies, having many points in common, as it is to separate a mixture of several fats.

[*To be continued.*]

[1] The first figure of each pair represents the appearance of a turbidity, the second figure the formation of flocks.

Contributions from the Chemical Laboratory of the Department of Agriculture, from H. W. Wiley.

XX.—ON THE NITROGENOUS BASES PRESENT IN THE COTTON SEED.

By W. Maxwell.

The nitrogenous bases choline and betaïne have been shown to be present in the cattle foods prepared from the cotton seed. Choline was discovered in a sample of those foods by Prof. R. Böhm, in the year 1881.[1] Böhm states having received from a druggist an alcoholic extraction of a cattle food prepared from cotton seed, which food, on being fed as a diet to young cattle belonging to a farmer in Germany, had proved fatally poisonous. From the "alcoholic extraction" a large preparation of choline was obtained; but Prof. Böhm concluded that no other alkaloidal principles were present.

In the year 1882 a preparation of betaïne was separated from the foods made from cotton seed by Prof. Ritthausen and Dr. Weger.[2] The discovery of the latter nitrogenous base, and admixed with unknown proportions of choline, has made it appear desirable that a revision of the investigations made by the given authorities should be undertaken, and particularly on account of the different toxical properties ascribed to choline and betaïne.

Prof. Gaehtgens, during experiments conducted in order to establish the toxical or non-toxical property of choline,[3] observed that when 0.3 gram of choline was given to a strong cat, an immediate paralysis occurred. Further, when 0.5 gram was administered to an equally vigorous cat, death was almost instantaneous. So far it has been believed that betaïne is a non-poisonous base; but the experiments made with betaïne, in respect of its toxical properties, could be revised with some advantage.

It has thus appeared important to determine whether choline or betaïne is present in the cotton seed, and the foods prepared from the seed in greatest quantity, and to estimate, approximately at least, the quantity of each of those bodies contained. And not only from a scientific standpoint is it desirable, but even more strongly so from a practical view, as the foods prepared from the

[1] Address before the Scientific Society in Marburg. [2] J. prakt. Chem. **30**.
[3] Dorpater med. Zeitschrift, Bd. I, 1870.

cotton seed are used very extensively as a common article of diet for cattle.

The investigations were conducted as follows: About five pounds of finely ground cotton-seed cakes were extracted with 70-per cent. alcohol. The reason for extracting the material with dilute alcohol instead of using very dilute solutions of mineral acid was to avoid any possible action of the acid upon the choline, by which means the latter could be in part converted into betaïne. After separation from the material, the extract was distilled and the residue taken up in water. The aqueous solution was treated with lead acetate, the lead precipitate separated by filtration, and the excess of lead removed from the filtrate and the latter evaporated down to a sirupy residue. This residue was then extracted with 70-per cent. alcohol containing 1-per cent. hydrochloric acid, in which menstruum the alkaloidal bodies were taken up. The alcohol-hydrochloric acid extraction was brought into a deep beaker, and an alcoholic solution of mercuric chloride added. Instantly on adding the mercuric chloride an almost pure, white double salt of the nitrogenous bases began to separate out.

After standing for 10 days a large preparation of the mercury-chloride double salts was separated from the liquid, the latter being set aside, and after standing some weeks a second crop of crystals was obtained. The double salts were dissolved in, and recrystallised out of, water, and after decomposition by means of hydrogen sulphide the sulphide of mercury was removed by filtration. The filtrate containing the hydrochlorates of the bases was very slowly evaporated to a small volume, and then placed in a desiccator over sulphuric acid until the crystallisation of the salts was complete. The hydrochlorate salts were free from color and in the form of lucid and well-developed crystals. After all moisture had been absorbed from the crystals they were saturated with an ample volume of absolute alcohol. In absolute alcohol the hydrochlorate of choline went into solution with some small portion of the betaïne salt. By this method an approximate estimation of the relative proportions of choline and betaïne was obtained.

In order to obtain a quantitative estimation of the relative proportions of choline and betaïne 7.248 grams of the hydrochlorate salts (water-free) were taken and treated with absolute alcohol. As it has been remarked, all the choline hydrochlorate salt was dissolved and some portion of the betaïne salt. The alcohol solu-

tion of the choline salt was evaporated to dryness and re-extracted with absolute alcohol three times, when it was found that the hydrochlorate of choline was obtained practically free from betaïne. The results obtained by this method of separation were as follows:

Choline hydrochlorate = 1.08 grams.
Betaïne " = 6.168 grams.

In the sample of cattle food, prepared from the cotton seed upon which this work has been done, the bodies choline and betaïne appear to be present in the following relative proportions:

Choline = 17.5 per cent.
Betaïne = 82.5 "

The alcohol solution of the hydrochlorate of choline was treated with platinum chloride, and, after recrystallisation of the precipitate, a fine preparation of the platinum double salt of choline was obtained. A portion of the platinum double salt was broken up by means of hydrogen sulphide, and, after separation of the sulphide by filtration, the water solution of the hydrochlorate of choline gave the following characteristic reactions:

With 1. Phospho-tungstic acid, white precipitate.
2. Phospho-molybdic acid, yellow precipitate.
3. Bismuth-potassium iodide, red precipitate.
4. Cadmium-potassium iodide, grey precipitate and was recrystallised.
5. Iodine, brown precipitate and was recrystallised.
6. Platinum chloride, yellow precipitate soluble in water.

The hydrochlorate of betaïne, after separation of the choline salt as already stated, was further treated in order to obtain a preparation of pure betaïne. The aqueous solution of the betaïne salt was treated with phospho-tungstic acid, when a phospho-tungstate of the base was obtained. The latter salt was broken up with calcium hydroxide, and the lime salt formed filtered off. The filtrate was evaporated to a residue and the latter was extracted with strong alcohol, out of which the free betaïne crystallised out. On recrystallising a purer preparation was obtained.

A further study will be made with the pure cotton seed, and of both the "Sea Island" and "Upland" varieties, in order to ascertain the comparative proportions of the nitrogenous bases present in the natural seed before it is subjected to expression of the oil and manufacture into cattle foods.

ELECTROMOTIVE FORCE OF METALLIC SALTS.

By C. L. Speyers.

Copper.

In continuation of a previous paper,[1] measurements of the electromotive force between copper and mercury in solutions of copper salts have been made, under my direction, in a most conscientious and able manner, by Mr. C. M. Hibbard, a senior student of the University.

For reasons previously stated, an amalgam was used, but, whereas a trifling addition of zinc to mercury gave it an electromotive force equal to that of zinc, a much larger amount of copper was required to effect a similar result. Most satisfaction was obtained by having pieces of amalgamated copper[2] floating in the amalgam; then the electromotive force of amalgam-mercury was sensibly equal to that of copper-mercury, provided no secondary action occurred, as evolution of hydrogen, formation of copper oxide, etc.; which secondary action, when not preventable, necessitated a replacement of the amalgam by a copper rod made of electrolytically deposited metal. This device does not do away with the thwarting action, but reduces its rapidity, for, when the amalgam was instantaneously affected, an appreciable time was required to corrode the copper surface. Amalgam measurements were made in the manner previously described, but the use of a rod involved a slight change in cell and manipulation. The mercury was contained in the tube, the stopper with its cup being replaced by a cork carrying the copper rod insulated by a glass tube. The deposit which formed on the rod was removed after each measurement by polishing with ground quartz and a clean rag, careful washing, and wiping with filter-paper. The liquids could be thoroughly mixed by shaking with a spiral motion.

Copper chloride was not available as an electrolyte, a film forming immediately upon the pure mercury, wherefore also all liquids containing this salt were excluded, as solutions of salts of copper and hydrochloric acid. Not so hydrochloric acid, alone or in combination with the other acids. The solutions were made by one of the methods previously described. To save space, only the mean increment, Δ, is given. Temperature between 20° and 25°.

[1] This Journal **12**, 254.

[2] The metal was obtained electrolytically.

v	$\frac{1}{4}$HCl.	$\frac{1}{4}HNO_3$.	$\frac{1}{4}$HAc.[1]	$\frac{1}{2}H_2SO_4$.	$\frac{1}{4}$HCl+ $\frac{1}{4}HNO_3$.	$\frac{1}{4}$HCl+ $\frac{1}{4}$HAc.
1	0.2564	0.3727	0.3595	0.3671	0.2324	0.2483
2	0 2437	0 4083	0.3590	0.3728	0.2252	0 2297
4	0 2288	0.4188	0.3586[2]	0.3889	0,2061	0.2034
8	0.2122	0.4303[3]	0.3586	0.3909	0.1978[5]	0.1898
16	0.2287[2]	0.4151	0.3546	0.3853	0.2074[6]	0.1999[2]
32	0 2363	0.4032	0.3595	0.3794	0.2282	0.2333
64	0.2391	0.3842	0.3534	0 3735	0.2350	0.2318
128	0.2390	0.3773	0.3506	0.3708	0 2356	0.2310
256	0.2354	.....	0.3440	0.3765[4]	0.2298	0.2298
512	.....	.....	0.3393	0 3887	0.2291	0.2298
	Δ = −0.0026	Δ = +0.0006	Δ = −0.0022	Δ = +0.0024	Δ = −0.0004	Δ = −0 0021

v	$\frac{1}{4}$HCl+ $\frac{1}{2}H_2SO_4$.	$\frac{1}{4}HNO_3$+ $\frac{1}{4}$HAc.	$\frac{1}{4}HNO_3$+ $\frac{1}{2}H_2SO_4$.	$\frac{1}{4}$HAc+ $\frac{1}{2}H_2SO_4$.	$\frac{1}{2}Cu(NO_3)_2$.[1]	$\frac{1}{2}CuAc_2$.[1]
1	0.2379	0.3888	0.3605	0.3690	.....	.....
2	0.2174	0.3558	0.3853[7]	0.3940	0.2316	0.1590
4	0 2000	0.3884	0.4035	0.4056[7]	0 2370	0.1323
8	0.1845	0.4006	0.3990	0 4130	0 2225[8]	0 1246
16	0 1610	0.4002	0 4151	0.4166	0.2366	0.1337
32	0.1600	0.4041	0 3976	0.4076	0 2267	0.1500[6]
64	0.1612	0.3943	0.4088	0.4068	0.2165	0.1573
128	0.1831[6]	0.3698	0.3823	0.3983	0.1925	0.1641
256	0.1985	0.3947	0.3816	0.4008	0.1841	0.1740
512	0.2142	0.3763	0 3780	0.3682	0.1690	.....
	Δ = −0.0016	Δ = +0 0055	Δ = +0 0010	Δ = −0 0001	Δ = −0.0078	Δ = +0.0021

v	$\frac{1}{2}CuSO_4$.[1]	$\frac{1}{2}Cu(NO_3)_2$+ $\frac{1}{2}CuAc_2$.[1]	$\frac{1}{2}Cu(NO_3)_2$+ $\frac{1}{2}CuSO_4$.[1]	$\frac{1}{2}CuAc_2$+ $\frac{1}{2}CuSO_4$.[1]	$\frac{1}{2}Cu(NO_3)_2$+ $\frac{1}{4}HNO_3$.	$\frac{1}{2}Cu(NO_3)_2$+ HAc.
1	0.2531	.....	.....	.....	.....	.....
2	0 2659[9]	0.1617[10]	0.2422	0.1771	0.2715	0.2466
4	0.2737	0.1515	0 2530	0.1761	0.2913	0.2605
8	0.2721	0 1371	0.2592	0.1913	0.3092	0.2795
16	0.2675	0.1528	0 2592	0.2159	0.3263	0 2927[7]
32	0.2630	0.1634	0.2550	0 2156	0.3311	0.3092
64	0.2569	0.1714	0.2440[9]	0.2234	0 3419	0.3217
128	0 2440	0.1718	0.2400	0.2224	0.3463	0.3203
256	0.2345	0.1668	0 2374	0.2171	0.3528	0.3269
512	.....	.....	.....	0.2074[11]	0.3364[7]	.....
	Δ = −0.0023	Δ = +0.0007	Δ = −0 0007	Δ = +0.0038	Δ = +0.0081	Δ = +0.0115

v	$\frac{1}{2}Cu(NO_3)_2$+ $\frac{1}{2}H_2SO_4$.	$\frac{1}{2}CuAc_2$+ $\frac{1}{4}HNO_3$.	$\frac{1}{2}CuAc_2$+ $\frac{1}{4}$HAc.[1]	$\frac{1}{2}CuAc_2$+ $\frac{1}{2}H_2SO_4$.	$\frac{1}{2}CuSO_4$+ $\frac{1}{4}HNO_3$.	$\frac{1}{2}CuSO_4$+ $\frac{1}{4}$HAc
1	.....	.....	.....	.....	0.2745	0.2592[8]
2	0.2791	0.2339	0.2037	0.2552	0.3086	0.2715
4	0.3067	0.2523	0 2099	0.2801	0 3234	0.2812
8	0.3247	0.2760	0.2214	0.3000[11]	0.3347	0.3027
16	0.3388	0.2956	0.2353[7]	0.3090	0.3466	0.3020
32	0.3476[11]	0.3138[6]	0.2410	0.3184	0.3540	0.3176
64	0.3704	0.3194	0.2586	0.3299	0.3604[10]	0.3277
128	0 3795	0.3212	0.2656	0.3306	0.3643	0.3335[7]
256	0 3687	0.3192	0.2809	0.3310	0.3683	0.3363
512	0.3698	.....	0.2914	0.3298	0.3679	.....
	Δ = +0.0113	Δ = +0.0122	Δ = +0.0109	Δ = +0.0093	Δ = +0.0104	Δ = +0.0097

[1] Copper rod in place of amalgam.
[2] 8 per cent. from mean.
[3] 2 " "
[4] 6 " "
[5] 9 per cent. from mean.
[6] 5 " "
[7] 14 " "
[8] 3 " "
[9] 7 per cent. from mean.
[10] 13 " "
[11] 4 " "

	$\frac{1}{2}CuSO_4 + \frac{1}{2}H_2SO_4$.	$\frac{1}{2}ZnCl_2$.	$\frac{1}{2}Zn(NO_3)_2$.	$\frac{1}{2}ZnAc_2$.[1]	$\frac{1}{2}ZnSO_4$.[1]	
1	0.3155	0.2489	0.3005	.....	0.2662	
2	0.3236	0.2482	0.3133	0.2565	0.2596	
4	0.3290	0.2194	0.3337	0.2608	0.2546	
8	0.3325	0.2073	0.3451	0.2652	0.2493[3]	
16	0.3510	0.2108	0.3236[2]	0.2549	0.2448	
32	0.3608	.....	.....	0.2487	0.2347	
64	0.3656	.....	.....	0.2440	0.2199	
128	0.3654	.....	.....	0.2296[3]	0.2078	
256	0.3707	.....	.....	0.2039	0.1991	
512	0.3559	.....	.....	0.1950	0.1957	
	$= +0.0045$	$\Delta = -0.0095$	$\Delta = +0.0058$	$\Delta = -0.0077$	$\Delta = -0.0078$	

Owing to tarnishing, these measurements are by no means so accurate as those with zinc. Judgment, sometimes rather arbitrary, was necessary, but fairly consistent results were obtained by taking the value immediately after the first rapid rise, before the rod had time to tarnish. When the rise was followed by a fall the highest value was recorded, for thereby most consistent results could be obtained. Whenever the deviation of either of a pair of measurements exceeded one per cent. of their mean, the determination was repeated and the average of four measurements given, with their maximum deviation added in a foot-note. In some cases this is very large, for the disturbing effect of oxidation is probably as great here as in the preceding zinc measurements, but the basis of calculation is much smaller. Notwithstanding we can readily perceive that:

1. The average increment is usually small; whenever large it is positive, except with copper nitrate and zinc chloride, acetate, and sulphate. But owing to the small initial value, dilution from $\frac{1}{2}$ equivalent to $\frac{1}{512}$ equivalent can increase the electromotive force over 43 per cent. ($\frac{1}{2}CuAc_2 + \frac{1}{2}HAc$), or with the amalgam, over 36 per cent. when diluted to $\frac{1}{256}$ equivalent ($\frac{1}{2}CuAc_2 + \frac{1}{2}HNO_3$).

2. The electromotive force in hydrochloric acid is lower than in the other three acids which form a group by themselves, the somewhat low value of acetic acid being doubtless connected with the use of the rod, for in its acid mixtures this acid acts like nitric and sulphuric acids.

3. The electromotive force in mixtures containing hydrochloric acid is the same or less, never markedly greater, than in hydrochloric acid alone. The other acids having an electromotive force nearly equal, their mixtures indicate little.

[1] Copper rod in place of amalgam. [2] 2 per cent. from mean. [3] 4 per cent. from mean.

4. Substitution of copper for hydrogen lowers the electromotive force very much, but excessive secondary action forbids numerical comparison.

5. In mixed solutions of two salts of different metallic and acid radicles, the electromotive force is only slightly greater than in the solution having the lower value, due consideration being taken of the weak nature of acetic acid.

6. The electromotive force in $\frac{1}{2}CuR + HR'$ is sensibly the same as in $\frac{1}{2}CuR' + HR$, the difference in concentrated solutions disappearing on dilution.

Iron.

An iron amalgam not being readily obtainable, the metal, as pianoforte wire, was arranged in a cork and the measurements performed exactly as with copper, and for a corresponding reason measurements in ferric chloride had to be omitted. Whenever the deviation from the mean was sensibly over one per cent., four measurements were made.

v	$\frac{1}{2}HCl$.	$\frac{1}{2}HNO_3$.	$\frac{1}{2}HAc$.	$\frac{1}{2}H_2SO_4$.	$\frac{1}{2}HCl + \frac{1}{2}HNO_3$.	$\frac{1}{2}HCl + \frac{1}{2}HAc$.	$\frac{1}{2}HCl + \frac{1}{2}H_2SO_4$.	$\frac{1}{2}HNO_3 + \frac{1}{2}HAc$.
1	0.5055	0.6992	0.8355[2]	0.8023[2]	0.4643[3]	0.5287	0.5113	0.6655
2	0.5227	0.7401	0.8399	0.8221	0.4717	0.5386	0.5238	0.6761
4	0.5415	0.7767	0.8411	0.8340	0.4873	0.5559	0.5547	0.7150
8	0.5734	0.8179	0.8673	0.8511	0.5699	0.5815	0.5817	0.7514
16	0.6013	0.8523	0.8829	0.8639	0.6249	0.6078	0.6184	0.8094
32	0.6231	0.8939[1]	0.8990	0.8748	0.6731	0.6395	0.6474	0.8600
64	0.6575	0.9257	0.9207	0.8902	0.7189	0.6701	0.6778	0.9076
128	0.6901	0.9479	0.9466	0.9068	0.7604	0.7107	0.7113	0.9430
256	0.7185	0.9548	0.9753	0.9639	0.8088	0.7961[2]	0.7655	0.9633
512	0.8241	0.9673	0.9815	1.0192	0.8504	0.8754	0.8141	0.9736
	$\Delta = 0.0354$	$\Delta = 0.0298$	$\Delta = 0.0167$	$\Delta = 0.0241$	$\Delta = 0.0429$	$\Delta = 0.0385$	$\Delta = 0.0370$	$\Delta = 0.0342$

v	$\frac{1}{2}HNO_3 + \frac{1}{2}H_2SO_4$.	$\frac{1}{2}HAc + \frac{1}{2}H_2SO_4$.	$\frac{1}{3}Fe(NO_3)_3$.	$\frac{1}{3}FeAc_3$.	$\frac{1}{6}Fe_2(SO_4)_3$.	$\frac{1}{3}Fe(NO_3)_3 + \frac{1}{3}FeAc_3$.	$\frac{1}{6}Fe_2(NO_4)_3 + \frac{1}{6}Fe(SO_3)_4$.
1	0.7087[4]	0.7800	.....	.....	0.9219	.....	.....
2	0.7352	0.8143	0.9323	0.8177	0.9391	0.8635	0.9346
4	0.7550	0.8327	0.9508	0.8826	0.9592	0.8910	0.9684
8	0.8092	0.8456	0.9708	0.8967	0.9723	0.9121	0.9959
16	0.8178	0.8603[2]	0.9601[2]	0.9059	0.9884	0.9405	1.0244
32	0.8704	0.8763	0.9607	0.9211	1.0010	0.9711[2]	1.0342
64	0.9114	0.8947	0.9809	0.9405	1.0322	0.9947	1.0485
128	0.9356	0.9160	1.0028	0.9785	1.0416	1.0031	1.0586
256	0.9492	0.9618	1.0112	1.0085	1.0395	1.0187	1.0695
512	0.9782	1.0237	1.0039	0.9592[4]	1.0610[5]	1.0100	1.0717
	$\Delta = 0.0300$	$\Delta = 0.0271$	$\Delta = 0.0089$	$\Delta = 0.0177$	$\Delta = 0.0154$	$\Delta = 0.0194$	$\Delta = 0.0171$

[1] 3 per cent. from mean. [2] 2 per cent. from mean. [3] 8 per cent. from mean.
[4] 4 per cent. from mean. [5] 5 per cent. from mean.

v	$\frac{1}{3}FeAc_3 + \frac{1}{6}Fe_2(SO_4)_3$.	$\frac{1}{3}Fe(NO_3)_3 + \frac{1}{3}HNO_3$	$\frac{1}{3}Fe(NO_3)_3 + \frac{1}{3}HAc$.	$\frac{1}{3}Fe(NO_3)_3 + \frac{1}{2}H_2SO_4$.	$\frac{1}{3}FeAc_3 + \frac{1}{3}HNO_3$.	$\frac{1}{3}FeAc_3 + \frac{1}{3}HAc$.
1	.....	.....	.....	.....	.....	.....
2	0.9443	0.8784	0.8411	0.8744	0.7855	0.8633
4	0.9498	0.9135	0.8678[4]	0.9144	0.8249	0.8875
8	0.9600	0.9460	0.8925	0.9460	0.8524	0.8961
16	0.9691	0.9662	0.9177	0.9734	0.8835	0.9078
32	0.9791	0.9666	0.9603	1.0048	0.9303	0.9176
64	0.9963	0.9798	0.9833	1.0300	0.9533	0.9358
128	1.0122	0.9922	0.9956	1.0280	0.9727[1]	0.9675
256	1.0571	1.0106	1.0131	1.0444	0.9838	1.0040
512	1.0765	1.0325	1.0120	1.0507	1.0027	0.9782
	$\Delta = 0.0165$	$\Delta = 0.0193$	$\Delta = 0.0214$	$\Delta = 0.0222$	$\Delta = 0.0217$	$\Delta = 0.0144$

v	$\frac{1}{3}FeAc_3 + \frac{1}{2}H_2SO_4$.	$\frac{1}{6}Fe_2(SO_4)_3 + \frac{1}{3}HNO_3$.	$\frac{1}{6}Fe_2(SO_4)_3 + \frac{1}{3}HAc$.	$\frac{1}{6}Fe_2(SO_4)_3 + \frac{1}{2}H_2SO_4$.	$\frac{1}{2}FeCl_2$.	$\frac{1}{2}Fe(NO_3)_2$.
1	.....	0.8309	0.9170	0.8900	.....	.. ...
2	0.9104	0.8754	0.9329	0.9074	0.6678	.....
4	0.9210	0.9150	0.9495	0.9289	0.6892	0.7979
8	0.9349	0.9390	0.9632	0.9475	0.7061	0.7830
16	0.9472	0.9727	0.9770	0.9610	0.6184	0.6410
32	0.9609	1.0012	0.9948	0.9707	0.6184	0.6674
64	0.9728	1.0205	1.0070	0.9775	0.6160[2]	0.6049
128	0.9912[1]	1.0362	1.0099	0.9945	0.6488	0.5883
256	1.0227	1.0419	1.0251	1.0058	0.6362	0.5938
512	1.0670	1.0684	1.0570	1.0329	.....	0.5904[3]
	$\Delta = 0.0196$	$\Delta = 0.0264$	$\Delta = 0.0156$	$\Delta = 0.0.60$	$\Delta = -0.0045$	$\Delta = -0.0296$

v	$\frac{1}{2}FeAc_2$.	$\frac{1}{2}FeSO_4$.	$\frac{1}{2}FeCl_2 + \frac{1}{4}HCl$.	$\frac{1}{2}FeCl_2 + \frac{1}{3}HNO_3$.	$\frac{1}{2}FeCl_2 + \frac{1}{4}HAc$.	$\frac{1}{2}FeCl_2 + \frac{1}{2}H_2SO_4$.
1	.....	0.8719	0.5165	0.4690[1]	.....	.....
2	0.4528	0.5013	0.5255	0.4681	0.5908	0.5537
4	0.5375	0.9152	0.5421	0.5305	0.7221	0.5710
8	0.5347	0.8567	0.5724	0.6025	0.7545	0.5942
16	0.6225[3]	0.8017	0.5967	0.6460	0.6822	0.6203
32	0.6918	0.7576	0.6277	0.7006	0.7147	0.6572
64	0.7312	0.7424	0.6678	0.7420	0.7619	0.6897
128	0.8192	0.6910[4]	0.7025	0.7760	0.8089[6]	0.7296
256	.....	0.6327	0.7630	0.8061	0.8469	0.7792
512	.....	0.6010	0.8474	.....	0.6927	0.8549[8]
	$\Delta = 0.0611$	$\Delta = -0.0300$	$\Delta = 0.0368$	$\Delta = 0.0421$	$\Delta = 0.0127$	$\Delta = 0.0377$

v	$\frac{1}{2}Fe(NO_3)_2 + \frac{1}{4}HCl$.	$\frac{1}{2}Fe(NO_3)_2 + \frac{1}{4}HNO_3$.	$\frac{1}{2}Fe(NO_3)_2 + \frac{1}{4}HAc$.	$\frac{1}{2}Fe(NO_3)_2 + \frac{1}{2}H_2SO_4$.	$\frac{1}{2}FeAc_2 + \frac{1}{4}HCl$.	$\frac{1}{2}FeAc_2 + \frac{1}{4}HNO_3$.
1	.....	.....	.....	.....	.....	.....
2	.....	.....	.....	.....	0.6181	0.7277
4	0.5272	0.7454	0.7495	0.7234[1]	0.6310	0.7621
8	0.6064	0.8102	0.7857	0.7892	0.6565	0.8014
16	0.6592[5]	0.8 07	0.8258	0.8296	0.6931	0.8415
32	0.6995	0.8936	0.8605	0.8648	0.7236	0.8843
64	0.7304	0.9209	0.8894	0.8994	0.7638	0.90 .7
128	0.7719	0.9363	0.9073	0.9265	0.8239	0.9251
256	0.8036	0.9514	0.9323	0.9186	0.8784	0.9352
512	0.8368	0.9441[7]	0.7387[7]	0.9679	0.7229[9]	0.7658[7]
	$\Delta = 0.0442$	$\Delta = 0.0284$	$\Delta = -0.0015$	$\Delta = 0.0351$	$\Delta = 0.0136$	$\Delta = 0.0048$

[1] 2 per cent. from mean. [2] 4 per cent. from mean. [3] 10 per cent. from mean.
[4] 6 " " " [5] 3 " " "
[7] 5 " " " [8] 7 " " "
[9] 8 " " "

v	$\frac{1}{2}FeAc_2 + \frac{1}{2}HAc.$	$\frac{1}{2}FeAc_2 + \frac{1}{2}H_2SO_4.$	$\frac{1}{2}FeSO_4 + \frac{1}{2}HCl.$	$\frac{1}{2}FeSO_4 + \frac{1}{2}HNO_3.$	$\frac{1}{2}FeSO_4 + \frac{1}{2}HAc.$	$\frac{1}{2}FeSO_4 + \frac{1}{2}H_2SO_4.$
1	.....	.....	0.5277	0.6911	0.7243	0.7505
2	0.6147	0.7871	0.5444	0.7414[4]	0.7435	0.7683
4	0.6632	0.8052	0.5649	0.7847	0.7687	0.7802
8	0.7068	0.8225	0.5944	0.8233	0.7933	0.8019
16	0.7591	0.8393	0.6235	0.8583	0.8143	0.8209
32	0.8031	0.8664	0.6550	0.8888	0.8446	0.8454
64	0.8651	0.8966	0.6872	0.9096	0.8735	0.8689
128	0.8930	0.9333	0.7200[3]	0.9301	0.9062	0.9165
256	0.9233	0.9601	0.7644	0.9557	0.9364	0.9457[3]
512	0.6841[1]	0.7799[2]	0.8466	0.9746	0.7839	1.0035
	$\Delta = 0.0087$	$\Delta = -0.0020$	$\Delta = 0.0354$	$\Delta = 0.0315$	$\Delta = 0.0066$	$\Delta = 0.0281$

v	$\frac{1}{2}FeSO_4 + \frac{1}{2}FeAc_2.$	$\frac{1}{2}FeSO_4 + \frac{1}{2}Fe_2(SO_4)_3.$	$\frac{1}{2}ZnCl_2.$	$\frac{1}{2}Zn(NO_3)_2.$	$\frac{1}{2}ZnAc_2.$	$\frac{1}{2}ZnSO_4.$
1	.....	0.8843	0.5795	0.7794	.....	0.8035
2	0.7537	0.9134	0.6171	0.8081	0.7568	0.8153
4	0.7727	0.9432	0.5742	0.8266	0.6876	0.8152
8	0.7821	0.9540	0.5774	0.8164[4]	0.6000[7]	0.8383
16	0.8101	0.9773	0.5970	0.6732	0.4790	0.8407
32	0.8381	1.0013	0.5920	0.6160	0.4692	0.8114
64	0.8546	1.0232	0.5381[5]	0.5716	0.4719	0.7720
128	0.8951	1.0420	0.5276	0.5308	0.4849	0.7276
256	0.8657	1.0629	0.5521	0.5310	0.4975	0.7669
512	0.6741[4]	0.9342[6]	.....	0.5237	0.4924	0.7352[6]
	$\Delta = -0.0099$	$\Delta = 0.0055$	$\Delta = -0.0034$	$\Delta = -0.0284$	$\Delta = -0.0330$	$\Delta = -0.0076$

Bearing in mind the uncertainty due to tarnishing—an uncertainty much less in most cases than with copper, both in percentage and in absolute value—it will be seen that:

1. The electromotive force always increases on dilution, except in solutions of the pure ferrous and zinc salts. Curious in behavior are solutions containing ferrous acetate, for the electromotive force rises in the usual manner to the 10th dilution, when a drop of from 140 to 240 millivolts occurs. Unfortunately, solutions of pure ferrous acetate decomposed so rapidly that beyond the 8th dilution no reliable measurements were obtainable. The result of this drop is to make the increment sometimes negative, but these cases are evidently different in nature from those in which it is negative throughout.

2. The electromotive force in hydrochloric acid is lower than in the other three acids, which again form a group by themselves, with nitric acid the lowest.

3. The electromotive force in equivalent mixtures containing hydrochloric acid equals or is less, never markedly greater, than

[1] 10 per cent. from mean. [2] 8 per cent. from mean. [3] 3 per cent. from mean.
[4] 2 " " " [5] 4 " " " [6] 35 " " "
[7] 23 " " "

that in hydrochloric acid alone. The other acids have an electromotive force so nearly equal that an equivalent statement cannot be demonstrated in their mixtures, yet it appears that the influence of that acid predominates in which the electromotive force is lowest. For in mixtures of nitric acid with acetic and sulphuric acids it is appreciably lower than in a mixture of the last two.

Ferric Salts.

4. Substitution of iron for hydrogen apparently raises the electromotive force, but the excessive secondary action, tarnishing of wire or mercury or decomposition of liquid, makes numerical comparison illusory.

5. In mixed solutions of two salts of different metallic and acid radicles, the electromotive force shows no regular dependence upon the constituents.

6. The electromotive force in $\frac{1}{2}FeR_3 + \frac{1}{2}HR'$ is not always equal to that in $\frac{1}{2}FeR'_3 + \frac{1}{2}HR$, especially in $\frac{1}{2}Fe(NO_3)_3 + \frac{1}{2}HAc$ and $\frac{1}{2}FeAc_3 + \frac{1}{2}HNO_3$. However, the color of the two mixtures showed that their constituents were not the same, but after heating for a couple of days to about 100° they were indistinguishable in color and electromotive force. Similarly with $\frac{1}{2}Fe_2(SO_4)_3 + \frac{1}{2}HAc$ and $\frac{1}{2}FeAc_3 + \frac{1}{2}H_2SO_4$.

Ferrous Salts.

4. The introduction of iron increases the electromotive force in three cases, but in the fourth diminishes it. However, in the latter the increment is strongly positive, while more or less negative in the other three, indicating a difference in the action of ferrous acetate on the one hand, and ferrous chloride, nitrate, and sulphate on the other. Moreover, the low electromotive force in the acetate is raised by the addition of acetic acid, so that when compared with the other ferrous salts correspondingly treated, the acetate assumes its proper position, and the chloride has the smallest value.

5. The electromotive force is lowest in solutions containing chlorine, excepting the ferrous acetate solution.

6. The electromotive force of $\frac{1}{2}FeR + HR'$ is equal to $\frac{1}{2}FeR' + HR$, when R is chlorine; otherwise the agreement is unsatisfactory, as in solutions of ferric salts.

Tin.

An amalgam was used in most of these measurements, the exceptions being noted. Tarnishing occurred only in nitric acid and in solutions of ferric sulphate and nitrate, but so violently in the last, that no value can be attached to the measurements in it. The tin rod substituted for the amalgam was treated in the same manner as the iron wire.

v	$\frac{1}{1}$HCl.	$\frac{1}{1}$$HNO_3$.	$\frac{1}{1}$HAc.	$\frac{1}{2}$$H_2SO_4$.	$\frac{1}{1}$HCl + $\frac{1}{1}$$HNO_3$.	$\frac{1}{1}$HCl + $\frac{1}{1}$HAc.
1	0.5840	0.8228	0.8467	0.8211	0.5860	0.5880
2	0.5880	0.7810[1]	0.8364[2]	0.8123	0.5994	0.5908
4	0.5864	0.7333	0.8015	0.8148	0.5834	0.6060
8	0.5946	0.7080	0.7911	0.7979	0.5998	0.6083
16	0.6127	0.7061	0.7876	0.7905	0.6272	0.6233
32	0.6250	0.6936	0.7838	0.7514[1]	0.6386	0.6350
64	0.6363	0.6690	0.7888	0.7334	0.6518	0.6465
128	0.6508	0.6488	0.8075	0.7079	0.6671	0.6699
256	0.6734	0.6690	0.8084	0.7056	0.6890	0.6947
512	0.6947	0.6936	0.8129	0.7008	0.7077	0.7223
	$\Delta = 0.0123$	$\Delta = -0.0144$	$\Delta = -0.0026$	$\Delta = -0.0134$	$\Delta = 0.0135$	$\Delta = 0.0149$

v	$\frac{1}{1}$HCl + $\frac{1}{2}$$H_2SO_4$.	$\frac{1}{4}$$SnCl_4$.	$\frac{1}{4}$$SnCl_4$ + $\frac{1}{1}$HCl.	$\frac{1}{4}$$SnCl_4$ + $\frac{1}{1}$$HNO_3$.	$\frac{1}{4}$$SnCl_4$ + $\frac{1}{1}$HAc.	$\frac{1}{4}$$SnCl_4$ + $\frac{1}{2}$$H_2SO_4$.
1	0.5975	0.5739	0.5760	0.5827	0.6022	0.5940
2	0.6032	0.5996	0.5956	0.5974	0.6150	0.5978
4	0.5891	0.6153	0.6117	0.6131	0.6244	0.6236
8	0.6119	0.6290	0.6207	0.6274	0.6304	0.6578
16	0.6344	0.6308	0.6197	0.6286	0.6423	0.6732
32	0.6488	0.6365	0.6292	0.6399	0.6530	0.6887
64	0.6602	0 6473	0.6456	0.6581	0.6625	0.6979
128	0.6791	0.6647	0.6572	0.6771	0.6773	0.7089
256	0.6977	0.6770	0.6752	0.6877	0.7067	0.7195
512	0.7181	0.7059	0.7046	0.7183	0.7472	0.7412
	$\Delta = 0.0134$	$\Delta = 0.0147$	$\Delta = 0.0154$	$\Delta = 0.0153$	$\Delta = 0.0161$	$\Delta = 0.0164$

v	$\frac{1}{2}$$SnCl_2$.[8]	$\frac{1}{2}$$SnCl_2$ + HCl.	$\frac{1}{2}$$SnCl_2$ + $\frac{1}{1}$$HNO_3$.	$\frac{1}{2}$$SnCl_2$ + $\frac{1}{2}$HAc.	$\frac{1}{2}$$SnCl_2$ + $\frac{1}{1}$$H_2SO_4$.	$\frac{1}{2}$$ZnCl_2$.
1	0.2883	0.3511	0.3990	0.3105	0.3743	0.6330
2	0.2945	0.3837[4]	0.3919	0.3000	0.3750	0.6734
4	0.2932	0.3796	0.3694	0.2933	0.3594	0.6947
8	0.2644	0.3525	0.3633	0.2926	0.3453	0.7123
16	0.2653	0.3446	0.4333[5]	0.3994[6]	0.3380	0.7149
32	0.2335	0.3463	0.5252	0.4328	0.3781	0.7270
64	0.2000	0.5109	0.5231	0.5056	0.4783[7]	0.7411
128	0.1900	0.5237	0.5328	0.4976	0.5327	0.7554
256	0.5184[3]	0.5227	0.5303	0.4958	0.5360	0.7768
512	0.5181	0.5637	0.5462	0.5175	0.5828	0.8018
	$\Delta = 0.0255$	$\Delta = 0.0236$	$\Delta = 0.0164$	$\Delta = 0.0230$	$\Delta = 0.0232$	$\Delta = 0.0188$

[1] 3 per cent. from mean.
[2] 5 per cent. from mean.
[3] 9 per cent. from mean.
[4] 7 " " "
[5] 17 " " "
[6] 35 " " "
[7] 93 " " "
[8] Tin rod.

v	$\frac{1}{2}Zn(NO_3)_2$.	$\frac{1}{2}ZnAc_2$.	$\frac{1}{2}ZnSO_4$.	$\frac{1}{3}Fe(NO_3)_3$.[3]	$\frac{1}{3}FeAc_3$.[3]	$\frac{1}{6}Fe_2(SO_4)_3$.[3]
1	0.6878	.....	0.8176	.....	.....	0.8949
2	0.6744[1]	0.8078	0.8221	0.8660	0.8869	0.9094
4	0.6796	0.8135[2]	0.8174	0 8559	0 8771	0.9090
8	0.6741	0.8016	0.8209	0.8559	0.8516	0.9044
16	0.7180	0.8161	0.8236	0.8458	0.8358	0.9044
32	0.7626	0 8213	0.8205	0 8053	0.8278	0.8988
64	0.7991	0.8310	0.8127	0.7666	0.8145	0.8913
128	0.8073	0.8217	0.8085	0.7666	0.8154	0.8611
256	0.8106	0.8279	0.8027	0.7666	0.8175	0.8321
512	0 8127	0.8218	0.8056	0.8154	0.8177	0.8254
	$\Delta = 0.0139$	$\Delta = 0.0018$	$\Delta = -0.0013$	$\Delta = -0.0063$	$\Delta = -0.0087$	$\Delta = -0.0077$

1. The electromotive force rises in general on dilution; in nitric and sulphuric acids, however, the increment is markedly negative. In the first case the amalgam tarnished when left in the liquid for some time, to avoid which the values had to be recorded, while still increasing, though very slowly, and in the second case the same was done to avoid tarnishing. In acetic acid the negative increment is very slight; both it and the somewhat larger numerical values in the iron solutions can be explained by a secondary action which was proven to exist in the solution of ferric acetate. A very curious occurrence is to be noted in solutions of stannous chloride, alone and with acids, a proceeding the reverse of that in ferrous acetate, for the electromotive force decreases to the 5th–9th dilution, when a sudden rise occurs. This is possibly due to formation of stannic salts; yet the solution of stannous chloride and nitric acid gave a precipitate with mercuric chloride at the 9th dilution. The 10th dilution of this liquid was not tested, but a solution of stannous chloride and acetic acid at this dilution gave a precipitate, proving in both cases the presence of stannous, though not the absence of stannic salt.

2. The electromotive force in hydrochloric acid is much lower than in the other acids, which latter form a group by themselves.

3. In mixtures of hydrochloric acid with other acids the electromotive force is the same as that in hydrochloric acid.

4. Substitution of stannic tin for hydrogen hardly changes the electromotive force, but substitution of stannous tin lowers it very much.

5. In mixtures of salts containing different metallic and acid radicles the electromotive force is determined by the constituent having the lower value.

[1] 3 per cent. from mean. [2] 4 per cent. from mean. [3] Tin rod.

Finally, the large deviations in the tables—15 to 35 per cent.—would mislead were the matter left unexplained. The aberrations occur where there is a rapid rise or fall and where the measurements have been made four times. Of these four, one generally takes the jump before the others, and therefore causes the wide departure from the mean, though before and after the jump all is regular.

The foregoing, taken collectively, clearly indicates the probability that the electromotive force is increased by dilution, even if it does not prove it. Is an explanation of this supposed law to be found in the dissociation or, better, *ionisation* hypothesis?—an hypothesis that asserts that a metallic salt in solution is partially separated into its ions, and that dilution increases the quantity thus separated or ionised, so that in a dilute solution no ions exist in combination. As yet no satisfactory explanation has been deduced. Ionisation increasing with dilution, the mean free path of each ion is lengthened; wherefore each atom, positive as well as negative, is less under the influence of the other, and appears, therefore, to impart more electricity to its electrode—to raise it to a higher potential. But this is hardly more than a statement of the above results in other words.

On the other hand, the ionisation hypothesis readily explains the production of electricity.[1] On introducing a metal into an electrolyte—an acid, for instance—both ions, in this case hydrogen and the acid radicle, will strike the metal. The negative ion will attract positive electricity, repelling negative, and go off with the metal in chemical combination, while the positive hydrogen ion will attract negative electricity, repelling positive, and thereby become neutral. But this does not continue indefinitely, nor until the metal is dissolved, for two reasons: first, the accumulated negative electricity gradually repels the negative ion, and finally altogether forbids its contact with the metal; secondly, the more negative the metal becomes the more hydrogen it attracts, which, accumulating on the surface, effectually shuts out the negative ion. The first is auxiliary rather than essential, for it is probable that before negative electricity could accumulate sufficiently altogether to repel the negative ions it would be carried off by the liquid, for a piece of gold leaf thrown into an aqueous solution of chlorine readily dissolves. The second, however, is very effective in bring-

[1] See Sohnke: Ztschr. phys. Chem. **3**, 1.

ing matters to a standstill. On introducing a second metal into the acid a similar process occurs, but not to the same extent, for there is cumulative evidence that elements differ in their relations to electricity, each allowing it to pass, but with diverse facility. So soon as electrical connection is established the potential of the two electrodes is equalised, and therefore diminished on one electrode and increased on the other. The result is that the negative ion which was in equilibrium with the electrode of lower negative potential is repelled, as the negative potential is increased, toward the electrode at first of higher negative potential, where also the equilibrium being disturbed by a reduction of negative potential, negative ions can again approach. At the same time the attraction for hydrogen is diminished, but is increased at the other electrode by the higher negative potential, and consequently hydrogen collects here. So long as electrical communication is kept up this state of things is continuously renewed, and a current produced and maintained by the partial discharge of the hydrogen ions and carrying off of electricity by the negative ions with the metal.

We shall assume that the positive and negative ions act very differently upon electricity, and by pushing this assumption we may reach a somewhat reasonable explanation of chemical affinity based upon the non-conductivity of the "non-metals" and the well known mutual attraction of positive and negative electricities. To do so we premise that the total quantity of electricity contained *within*[1] any given mass of an element is constant (possibly it may vary as the equivalence, but for the present this is to be left undecided); that in metals and other good conductors this electricity may be all positive electricity, or positive and negative. When these are present in equal quantities the atom is neutral. The non-metals are non-conductors and contain negative electricity. Their atoms are like spheres surrounded by an insulating shell within which is one or more charges of negative electricity. When such an atom comes in contact with a metal the positive electricity is attracted, the negative repelled; but as the electricities cannot unite owing to the insulation of the negative ion, a quantity of matter containing the same number of unit-charges of *positive* electricity is carried off with it in so-called "chemical combination." Wherefore, the better the

[1] This excludes any artificial charge to be found on the surface.

insulation of the negative ion and the less negative electricity in the positive ion, the more firmly[1] are the ions chemically united. In accordance herewith combinations of metals should be weak; likewise those of non-metals, owing to the presence of negative electricity. But a combination of a non-conductor or insulator with an excellent conductor should be strong, and this idea experience confirms.

The separation of this electricity consumes energy and, as indicated in a previous paper, we might expect to find the chemical energy, as measured by heat, equal to that consumed in the separation. In order that this equality may exist the performance of other internal work is impossible; but as internal work generally exists, the equality is exceptional. Helmholtz has indeed demonstrated the matter, though not in this form. By thermodynamical manipulation he has shown[2] that whenever the electromotive force is a function of temperature the two energies in question are not equal, but that the relation between heat (Q), internal energy (U), temperature (T), electromotive force (ϕ), and quantity of electricity (e), is

$$dQ = \frac{\delta U}{\delta T} dT + \frac{\delta \phi}{\delta T} de.$$

Yet since this demonstration requires the aid of the second law of thermodynamics,

$$\int \frac{dQ}{T} = 0,$$

the first equation is only strictly applicable to reversible cells; however, the principle involved therein, that the internal energy must be considered, is of universal application. Hence the futility in expecting to find the chemical and electrical energies numerically equal, and this is well shown by a comparison, so far as thermal data will permit, of the calculated and observed electromotive forces of zinc, copper, iron, tin and mercury in solutions of hydrochloric and nitric acids.

If the electrodes are electrically disconnected we have

$$M\left\{\begin{matrix} H \\ Cl \end{matrix} + HClAq + \begin{matrix} H \\ Cl \end{matrix}\right\} Hg, \text{ and}$$

$$M\left\{\begin{matrix} H \\ NO_3 \end{matrix} + HNO_3Aq + \begin{matrix} H \\ NO_3 \end{matrix}\right\} Hg.$$

[1] Used in the ordinary sense.

[2] Gesammelte Abhandlungen **3**, 961.

Accordingly, each electrode tending to produce a current in opposite directions, the difference of the chemical energies is to be taken as the measure of electromotive force. We have from Thomsen's data:[1]

$$\tfrac{1}{2}Hg + HClAq = \tfrac{1}{2}HgCl_2Aq + \tfrac{1}{2}H_2 - 14350 \text{ cals.},$$
$$\tfrac{1}{2}Zn + HClAq = \tfrac{1}{2}ZnCl_2Aq + \tfrac{1}{2}H_2 + 17120 \text{ cals.},$$
$$\tfrac{1}{2}Cu + HClAq = \tfrac{1}{2}CuCl_2Aq + \tfrac{1}{2}H_2 - 7945 \text{ cals.},$$
$$\tfrac{1}{2}Fe + HClAq = \tfrac{1}{2}FeCl_2Aq + \tfrac{1}{2}H_2 + 3270 \text{ cals.},$$
$$\tfrac{1}{2}Fe + HClAq = \tfrac{1}{2}FeCl_2Aq + \tfrac{1}{2}H_2 + 10675 \text{ cals.},$$
$$\tfrac{1}{4}Sn + HClAq = \tfrac{1}{4}SnCl_4Aq + \tfrac{1}{2}H_2 - 7 \text{ cals.},$$
$$\tfrac{1}{2}Sn + HClAq = \tfrac{1}{2}SnCl_2Aq + \tfrac{1}{2}H_2 + 1270 \text{ cals.}$$

The energy-equivalent of one calorie is $4153 \cdot 10^4$ c. g. s. units; hence the energy (W) of the above reactions is

$$W = \text{cals. } 4153 \cdot 10^4.$$

Now as one unit of electricity, or one coulomb, is contained in 0.001118 gram of silver, one gram-equivalent of this metal or any other substance contains

$$0.001118 \cdot 107.94 = 96540 \text{ coulombs.}$$

The energy consumed in producing this quantity of electricity is determined by its electric height, or electromotive force, that is,

$$W = 96540 \,.\, EF = EF \cdot 9654 \text{ c. g. s. units.}$$

On combination with the above equation,

$$EF = \frac{\text{cals. } 4153 \cdot 10^4}{9654 \cdot 10^4} = \text{cals. } 4302 \cdot 10^{-8}.$$

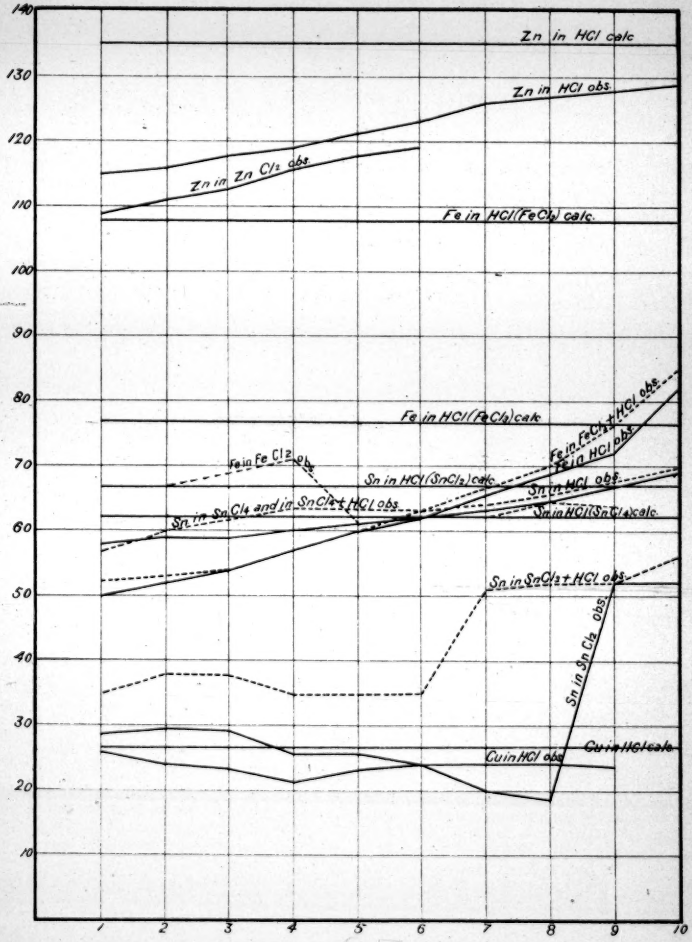
Wherefore for zinc the electromotive force should be

$$EF = 0.00004302 \cdot (17120 + 14350) \text{ cals.} = 1.35 \text{ } V.$$

Similarly, for copper $= 0.27$ V, for ferric iron $= 0.76$ V, for ferrous iron $= 1.08$ V, for stannic tin $= 0.62$ V, and for stannous tin $= 0.67$ V. These results are plotted in the accompanying Diagram No. 1 as straight lines.

The curved lines represent the observed electromotive force in hydrochloric acid and in solutions of the corresponding chlorides.

[1] Thermochemische Untersuchungen.


Zn in HCl calc
Zn in HCl obs.
Zn in Zn Cl2 obs.
Fe in HCl(FeCl2) calc.
Fe in HCl(FeCl3) calc.
Fe in Fe Cl2 obs.
Fe in Fe Cl3 + HCl obs.
Fe in HCl obs.
Sn in HCl(SnCl2) calc.
Sn in HCl obs.
Sn in SnCl4 and in SnCl2 + HCl obs.
Sn in HCl(SnCl4) calc.
Sn in SnCl2 + HCl obs.
Sn in Sn Cl4 obs.
Cu in HCl obs.
Cu in HCl calc.
140
130
120
110
100
90
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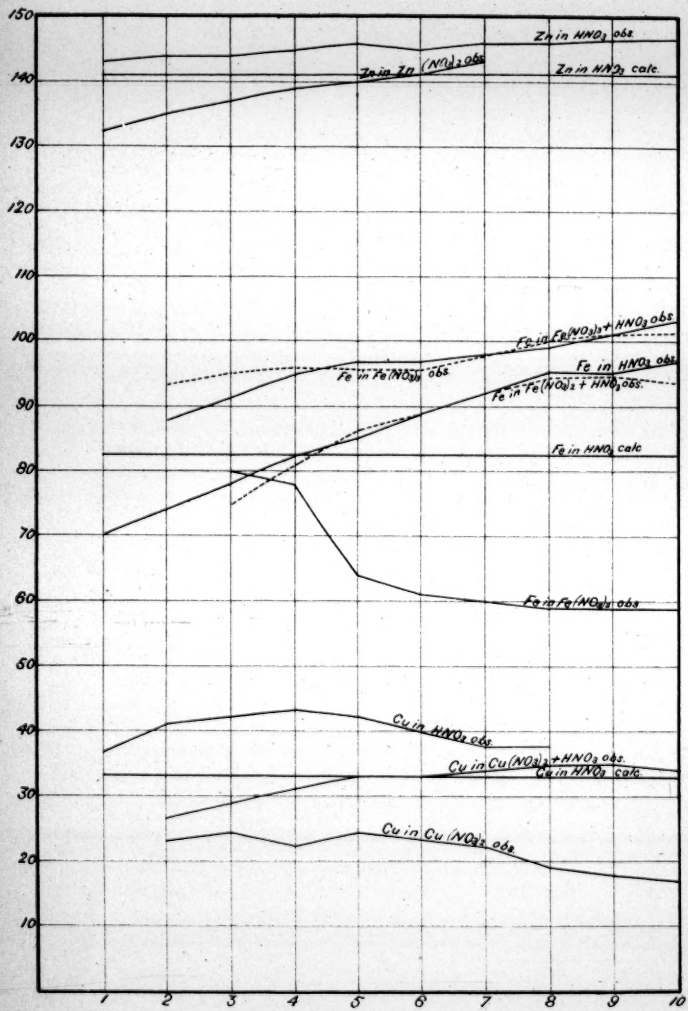
150
140
130
120
110
100
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1
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7
8
9
10
Zn in HNO3 obs.
Zn in Zn(NO3)2 obs.
Zn in HNO3 calc.
Fe in Fe(NO3)2 + HNO3 obs.
Fe in Fe(NO3)2 obs.
Fe in HNO3 obs.
Fe in Fe(NO3)2 + HNO3 obs.
Fe in HNO3 calc.
Fe in Fe(NO3)2 obs.
Cu in HNO3 obs.
Cu in Cu(NO3)2 + HNO3 obs.
Cu in HNO3 calc.
Cu in Cu(NO3)2 obs.

Results are also given for the nitrates in No. 2, where

$$\tfrac{1}{2}Hg + HNO_3Aq = \tfrac{1}{2}Hg(NO_3)_2Aq + \tfrac{1}{2}H_2 - 15665 \text{ cals.}$$
$$\tfrac{1}{2}Zn + HNO_3Aq = \tfrac{1}{2}Zn(NO_3)_2Aq + \tfrac{1}{2}H_2 + 17055 \text{ cals.}$$
$$\tfrac{1}{2}Cu + HNO_3Aq = \tfrac{1}{2}Cu(NO_3)_2Aq + \tfrac{1}{2}H_2 - 7995 \text{ cals.}$$
$$\tfrac{1}{3}Fe + HNO_3Aq = \tfrac{1}{3}Fe(NO_3)_3Aq + \tfrac{1}{2}H_2 + 3316 \text{ cals.}$$

Accordingly the calculated electromotive force should for zinc = 1.41 *V*, for copper = 0.33 *V*, and for iron = 0.82 *V*.

The curves show that although there is a general analogy between electromotive force and chemical energy, the two are by no means equal.

Particularly interesting is the difference in electromotive force between the *-ous* and *-ic* compounds. The heats of formation of *-ous* salts are probably greater, for equivalent quantities, than those of *-ic* compounds, and consequently, the calculated electromotive forces also should be higher. Yet the observed values of the *-ous* salts are lower. True, it may be urged that a minute quantity of an *-ic* salt is formed and consequently the value depreciated, as this is in general controlled by the lower electromotive force. But the conditions are all unfavorable to the formation of these compounds, and with iron and tin, only *-ous* chlorides are obtained by the processes supposed to take place in the cells. Can we find an explanation in the dissociation hypothesis and the one above?

As non-conductors have negative electricity so interwoven in their texture that very little, if any, motion of electricity can take place within the atom, when such an atom approaches and touches a mass of metal the negative ion will attract a quantity of the positive ion containing a unit charge and go off with it as a chemical compound. This, as containing the largest quantity of metal, will be the *-ous* compound. Before migrating far it will meet negative ions, and possessing a comparatively large charge of positive electricity, may give up a part, but never without accompanying matter, to the second negative ion, thus forming a compound relatively richer in negative ion or an *-ic* compound. The quantity of electricity in the positive ion of this being so much less than in the positive ion of an *-ous* salt, when a quantity of an *-ic* salt is formed equivalent to one atom of the negative ion the heat evolved is necessarily much less than that yielded in the formation of a corresponding quantity of an *-ous* salt.

Again, in the preceding explanation of electromotive force a

dynamical equilibrium was supposed—an equilibrium resulting from a charge of the electrode with negative electricity by the negative ion and a partial removal of that electricity by the positive ion. As the charge of the positive ion is much smaller in the *-ic* condition, the electricity removed is also much less, and the potential is therefore higher. Of course the action is similar on both electrodes, but the electrode least affected in the first case is presumably least affected in the second, and the result is an increased difference of potential or rise of electromotive force.

In this or some similar way it seems that an explanation is to be found; whether it will suffice for all cases future experiments alone can decide. A change of internal energy in the way of dissociation must not be overlooked, but it is hard to think that this can account for such a difference of electromotive force as is observed in solutions of *-ous* and *-ic* salts.

It would therefore be of great interest to extend determinations to all metallic salts, more especially to metals forming *-ous*, *-ic* and *per-* salts, and to determine if there are any solutions in which dilution lowers the electromotive force while secondary action is excluded. But other work, in the meantime begun, will demand attention, so that these results are now published in the hope that some one will feel inclined to carry the matter farther.

UNIVERSITY OF MISSOURI, *June*, 1891.

NOTES ON DIAZOBENZENE PERBROMIDE.[1]

BY CHARLES E. SAUNDERS.

This work was undertaken for the purpose of studying the conduct of diazobenzene perbromide and of triazobenzene (diazobenzene-imide of Griess) towards various reagents, and especially the products obtained by treating the former substance with substituted ammonias, as it appeared highly probable that the work of Griess[2] in this direction had not been correctly interpreted by him. Shortly, however, after the commencement of the investi-

[1] The author wishes to express his sincere thanks to Professor Remsen for his kindness in directing the work of which an account is here given.

[2] Phil. Trans. 1864, 673.

gation an article[1] was published in one of the journals, from which it appeared that somewhat similar work was being carried on elsewhere, so that it seemed best not to continue the research in the direction originally intended. Nevertheless a few observations which may be worthy of notice were made.

Preparation of Diazobenzene Perbromide.

The most convenient method found was to prepare diazobenzene sulphate according to the method of Knoevenagel,[2] dissolve in a little water, filter quickly, and then add with constant stirring an excess of a cold solution of bromine in moderately concentrated hydrobromic acid. The perbromide separates under these circumstances as a dark-colored, pasty mass which can easily be removed from the aqueous solution of the acid. By washing with several portions of pure ether the perbromide is partly purified and is obtained as a reddish-brown solid with a strong bromine-like odor. By exposing this solid, spread out on drying-paper, to the air for about an hour the odor disappears almost entirely and the color of the substance fades to a yellowish-brown. It is then in a condition fit for use. When prepared according to the method of Griess—using a solution of bromine in quite dilute hydrobromic acid—the crude product is precipitated as a dark liquid much like bromine. This seems to have been regarded by Griess as a comparatively pure product. It appears probable, however, that this liquid condition is due to the presence of more bromine than is required by the formula $C_6H_5N_2Br_3$. In support of this may be mentioned the fact, observed by Griess, that the perbromide can be obtained in solid condition by treating the liquid product with ether. That author does not explain this action of ether, but it seems to be most easily understood by supposing that the solvent removes the excess of bromine from the liquid and thus allows the perbromide to separate in its natural condition. It may be, however, that the ether dissolves out some definite chemical compounds formed between bromine and diazobenzene perbromide, and which, while present, keep the remainder of the perbromide in a liquid state. The ether used for washing the liquid or pasty perbromide always becomes highly colored as if by bromine.

[1] Gaz. Chim. It. **20**, 798.

[2] Ber. d. chem. Ges. **23**, 2994.

In the present investigation a further fact was discovered bearing on this point. When pure, dry diazobenzene perbromide is subjected to the action of bromine vapor, mixed with air, at ordinary temperatures it takes up bromine and is rapidly converted into a liquid. If the action be not allowed to go very far the perbromide can be recovered, in part, in solid condition by treatment with ether. Quantitative experiments were made for the purpose of determining whether by the action of bromine vapor a liquid compound of definite composition could be obtained. This was not found possible. The proportion of bromine taken up varies with the amount of air mixed with the vapor. In one experiment where air was almost entirely absent the perbromide took up several times its weight of bromine in twenty-four hours. The method of treatment in this case was to place a beaker containing the solid perbromide beside a beaker containing bromine. The two were then covered with a bell-jar which was almost air-tight. Under these circumstances 1.0655 grams of solid perbromide took up 3.9493 grams of bromine.

While these experiments failed to prove the formation of any single, definite compound, there seems to be no doubt that bromine enters into combination with diazobenzene perbromide. It appears, therefore, highly desirable that in all experiments with this substance it should be first of all purified by washing with ether and obtained in dry condition. Symmetrical tribrombenzene was the only other impurity recognised in the perbromide as obtained in pasty condition by the method described. It was identified by a careful comparison with the product obtained from tribromaniline. Washing the perbromide by rubbing it up in a mortar containing ether will remove the tribrombenzene, but not without difficulty.

Decompositions of Diazobenzene Perbromide.

On being allowed to stand in bromine water, it forms tribromphenol. Hence a considerable amount of this product is formed by allowing the contents of the beaker in which the perbromide has been made to stand over night. The reaction takes place quickly if the solution is heated.

When diazobenzene perbromide is boiled with pure water the chief products formed are tribromphenol, phenol, hydrobromic acid, free nitrogen and free bromine. The tribromphenol was

identified by comparison with the substance as obtained directly from phenol by the action of bromine water.

The presence of phenol was proved by the color-reactions of, and the action of bromine water on, the distillate obtained by passing steam through the original liquid.

According to Griess, when diazobenzene perbromide is warmed with alcohol there is formed, almost quantitatively, monobrombenzene. This observation appears to be incorrect. By heating the perbromide with absolute alcohol to boiling, adding water, and then distilling with water-vapor, a heavy oil was obtained, which was dried by calcium chloride and then subjected to fractional distillation. It was easily separated into two principal portions, one of which boiled at 155°–157° and was evidently monobrombenzene, while the other boiled considerably above 200°. After several distillations, that fraction of the high-boiling product was taken which passed over between 228° and 233° (uncorr.). The percentage in this was then determined by the method of Carius, the heating being carried on for fourteen hours at about 170°. 0.2930 gram substance gave 0.2790 gram AgBr, which represents 40.52 per cent. of bromine, the amount required by the formula $C_6H_4BrOC_2H_5$ being 39.80 per cent. Lippmann[1] obtained monobromphenetol by the action of bromine on phenetol and also by the action of the potassium salt of (para)bromphenol on ethyl iodide. He gives the boiling-point of the product as 233°. It is evident, therefore, that the substance obtained in this case was parabromphenetol, identical with that of Lippmann, though the analysis and the variation in boiling-point show that it was not pure. The bromphenetol was found very difficult to solidify. It was solidified, however, by the action of solid carbon dioxide and ether. Its melting-point proved to be +4°. This had not been previously determined.

The decomposition of the perbromide by hot alcohol was performed a number of times, and bromphenetol was always found to be produced in considerable quantity. Brombenzene formed, as a rule, less than one-half of the total liquid products by volume. It appears, therefore, that when hot alcohol acts on diazobenzene perbromide, the chief products of the reaction are parabromphenetol and monobrombenzene. Hydrobromic acid and free nitrogen are of course formed, as well as several other substances

[1] Wien. Akad. Ber. (2 Abth.) **62**, 611.

both solid and liquid. The formation of a phenetol derivative in this case accords with the observation of Remsen and Orndorff,[1] that diazobenzene nitrate when heated with alcohol gives a very large proportion of phenetol, and not simply benzene as first stated by Griess. Many other examples of the formation of ethoxy compounds under similar circumstances might be cited.

When the perbromide is kept for several hours in boiling ether, brombenzene is formed in considerable quantity. With glacial acetic acid it is also formed, though in smaller proportion, and associated with another liquid (possibly a brom-phenyl acetate) of much higher boiling-point. On standing in a desiccator over caustic potash the perbromide gradually decomposes with loss of color. The products formed were not investigated. In general terms it may be said that diazobenzene perbromide has a decided tendency to yield monobrombenzene as one of its decomposition products, but that almost all of the reactions in which it is involved result in the formation of too many products to render the substance very useful in chemical investigations.

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REVIEWS AND REPORTS.

RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.

V.—*Ammonia, Nitric Acid, Explosives.*

Ammonia.

Sources.—Practically all the ammonia of commerce, which in the form of sulphate finds extensive use as a fertilizer, is still obtained from the nitrogen of coal. Nearly the whole of that obtained from this source is prepared from the ammoniacal liquor of the gas-works, and but little progress has been made in the direction of regaining the immense quantities of ammonia given off in the combustion of coal as fuel.

Most varieties of coal contain 1.3–1.5 per cent. of nitrogen.

[1] This Journal **9**, 387.

According to Lunge,[1] assuming the total quantity of coal burned to be 400 million tons, this would be equivalent, if all the nitrogen could be obtained as ammonia, to 26 million tons of ammonium sulphate, or about 200 times the total amount actually obtained. More than 90 per cent. of this coal is, however, burned as fuel under conditions which make the recovery of the nitrogen as ammonia very difficult. From the portion used in gas-making, also, only about one-seventh of the nitrogen contained in the coal is practically obtained in the form of ammonia, the remainder chiefly remaining in the coke or passing off as free nitrogen.

Smaller quantities of ammonia are also obtained from the gases given off from coke-ovens and blast-furnaces, and in the distillation of shale. The following table, taken from the reports of the English Alkali-Inspector, gives the relative amounts of ammonium sulphate obtained in Great Britain from these various sources within the past four years:

	1886. Tons.	1887. Tons.	1888. Tons.	1889. Tons.
Gas works	82,500	85,000	93,000	100 000
Iron works	4,000	5,000	5,300	6,000
Shale distilling works . . .	18,000	21,000	22,000	23,000
Coke and carbonising works,	2,000	2,700	2,500	3,000

While it appears practically out of the question to save the ammonia yielded when coal is burned directly for heating purposes, there are two methods of using coal as fuel in connection with which immensely increased quantities of ammonia might easily be obtained; these are the manufacture of coke in coke-ovens, and the production of gaseous fuel. From these sources we may expect to see in the future the great increase in the world's production of ammonia.

The amount of coal converted into coke, chiefly for metallurgical purposes, is not far from 10 per cent. of the total coal produced. If we assume that the amount so treated is 40 million tons, and that 20 lbs. of ammonium sulphate are obtained from one ton of coal, we find that if all the ammonia given off in the coking of coal were regained, not less than 400,000 tons of ammonium sulphate would be obtained from this source. Nearly all the coke produced is, however, made in *bee-hive* or similar ovens, in which the gaseous products and a portion of the coal are burned in order to carbonise the remainder; with these ovens the saving of the ammonia is impracticable. Flue-ovens, in which the coal is coked in closed chambers by the heat of the burning gas circulating through flues in the side walls, like those on the *Coppée* or *Simon-Carvès* system, have been introduced to some extent in Europe, and their use is gradually extending. These permit the recovery of the ammonia and tar given off; the chief

[1] Thorpe's Dict. "Ammonia."

obstacle to their adoption has, however, been their high first cost. In this country several attempts have been made to use this form of oven and recover the by-products, but these attempts have always been abandoned. Certain forms of flue-oven have been greatly cheapened and simplified during the past few years, and have proved very successful and economical in Germany, so that the introduction of this improved process in this country, with production of ammonia as a by-product, is probably only a question of time.

The possibility of obtaining ammonia as a profitable by-product in the conversion of coal into fuel-gas in gas-producers has lately been demonstrated by the experiments of Mond.[1] It was found that a good yield of ammonia could only be obtained by keeping the temperature in the producers very low, and by the use of an amount of steam equal to about twice the weight of the coal consumed. Under these circumstances about half the nitrogen is obtained in the form of ammonia, giving a yield of 70 pounds of sulphate per ton, or more than three times the yield commonly obtained in the gas-works. Mond's process, which is in operation on a large scale at the soda-ash works at Norwich, England, is fully described in the paper to which reference is given. Very complicated apparatus is required for the cooling of the large volume of gas produced, the condensation of the steam, and the absorption of the ammonia by acidified ammonium sulphate solution. The fuel-gas obtained contains, by percentage, 15 of carbon dioxide, 10 of carbon monoxide, 23 of hydrogen, 3 of hydrocarbons, and 49 of nitrogen. It is therefore of somewhat lower heating power than ordinary producer-gas. According to Mond, its calorific power is equal to 73 per cent. of that of the coal from which it is made. The actual cost of the ammonium sulphate produced, including fuel consumed, labor, etc., is about £5 per ton, or less than half the present price in England. The cost of the plant is very considerable, and it is stated that the process can be successfully worked only by large consumers of cheap fuel. Mr. Mond remarks that if only one-tenth of the fuel consumed in England were treated by this process, that country could supply an amount of sulphate of ammonia equivalent to the whole quantity of that salt and of nitrate of soda used in the Old World for fertilising purposes.

Fixation of Atmospheric Nitrogen.—Attempts have long been made to bring the nitrogen of the air into combination with carbon or hydrogen and thus obtain cyanides or ammonia. The history of these experiments has lately been fully reviewed by Breneman[2] and by Fawsitt.[3] The only methods which have yielded any encouraging results consist in passing nitrogen over white-hot charcoal previously saturated with an alkali; a cyanide is thus produced

[1] J. Soc. Chem. Ind. (1889), 505. [2] J. Amer. Chem. Soc. **11**, 1–45.
[3] J. Soc. Chem. Ind. (1890), 30.

which, if ammonia is desired, may be subsequently decomposed by steam. The process of Possoz and Boisière was carried out in 1843 on a manufacturing scale by Bramwell & Hughes of Newcastle. Fire-clay retorts were filled with wood-charcoal previously impregnated with potassium carbonate; after raising the retorts to a white heat, air was passed through them for a certain time, the contents were then cooled, lixiviated, and the cyanide obtained converted into ferrocyanide by treatment with ferrous sulphate. In this way two tons per week of ferrocyanide were obtained from a bench of eight retorts. From a commercial point of view the process was a failure, owing to loss of potash and wear and tear of the plant; it was therefore abandoned in 1847. A similar process employed by Fawsitt, using sodium carbonate with a view to the production of ammonia, led to equally unsatisfactory pecuniary returns.

Mond[1] has recently made experiments on a manufacturing scale with the process of Marguerite and Sourdeval (Eng. pat. 1860), in which barium carbonate is the alkali employed. This was made into balls with charcoal and pitch; after calcining in a reducing flame the balls were charged into vertical fire-clay retorts heated to a temperature of 1400° C., and submitted to the action of a current of nitrogen obtained from the carbonating towers of the ammonia-soda process. After a certain time about 40 per cent. of the barium oxide present was converted into cyanide; the briquettes were then dropped into a closed cooling-chamber and finally treated with steam, by the action of which ammonia was formed and the carbonate regenerated. Owing to the difficulty of securing fire-clay retorts which would resist the high temperature employed, Mr. Mond was obliged to abandon the experiments; he is, however, of the opinion that the difficulties can be overcome, and that the process will prove remunerative for the manufacture of cyanides.

Nitrates.

Until twenty years ago nearly all the saltpetre, or potassium nitrate, of commerce was obtained from India, where it is collected in the form of an incrustation upon the soil in thickly populated regions, arising from the gradual oxidation of animal organic matter. The supply of saltpetre from this source has decreased, and now amounts to about 25,000 tons per year. A large quantity of saltpetre was also made in this country, in the early part of this century, by leaching the earthy matter dug up in caves, chiefly in the Mammoth Cave, Ky.

The deposits of sodium nitrate, or Chili saltpetre, near the seacoast of Chili, in the province of Tarapaca and the desert of

[1] Loc. cit.

Atacama, have lately been fully described in a most interesting report by Consul Walker, of Bogota.[1] These deposits have been known and worked for nearly seventy years. They extend a distance of 260 miles along the coast, and have in some places a depth of over six feet. The total amount of available material has been estimated to be 178 million tons. The presence of 20 per cent. of salt and 0.05 per cent. of iodine in the mineral indicates that it has been formed by the gradual oxidation of the nitrogenous matter of seaweed. The "caliche" is refined by recrystallisation from water, and comes into commerce 95–98 per cent. pure. The exportation of nitrate of soda from Chili amounted in 1888 to 785,000 tons (of 1000 kilos), and in 1889 to 921,000 tons. By far the larger part of this product is used in agriculture.

Potassium nitrate is now chiefly obtained by treating the Chili nitrate of soda with potassium chloride from Stassfurt. More than 50,000 tons of the nitrate of soda produced in 1888 was used for this purpose, and Pfeiffer[2] states that 41.2 per cent. of the potassium chloride produced at Stassfurt is employed in this industry. The production of potassium chloride in 1888 was 123,550 tons; 41.2 per cent. of this is 51,000 tons, which would correspond to an annual production of nearly 70,000 tons of artificial saltpetre.

Explosives.

The most recent advances in the manufacture of explosive materials have lately been summed up in an interesting manner in papers by Abel[3] and McRoberts.[4]

All explosive compounds hitherto used for fire-arms and ordnance have possessed two defects, viz. too rapid combustion, and the evolution of dense volumes of smoke. The efforts of inventors during the past decade have largely been expended in the direction of overcoming these drawbacks.

Gunpowder, which burns with moderate rapidity, produces more smoke than other explosives. Nearly 50 per cent. of the products of combustion of gunpowder are non-gaseous, and the white smoke produced consists chiefly of potassium carbonate, sulphate and sulphide, in a state of fine division. This large proportion of solid products adds greatly to the corrosion of the bore of the gun. Nobel's experiments have shown that those substances which on explosion liberate the largest proportion of gas and develop the least heat produce the least corrosive effect.

The rapidity of combustion of gunpowder may be to a considerable extent decreased by moulding into larger grains and submitting these to heavy pressure, as is commonly the practice in the manufacture of powder for heavy guns. A further advance

[1] U. S. Consular Reports, No. 114, March, 1890.
[2] Chem. Industrie (1888), 129.
[3] Royal Institution Lecture, Jan. 31, 1890.
[4] J. Soc. Chem. Ind. (1890), 476.

in this direction is the introduction of the brown "cocoa-powder," which has lately come into extensive use in Germany. This contains much more saltpetre and less sulphur than ordinary gunpowder; the charcoal it contains is also but slightly burned, and gives the powder a brown shade. This explosive burns more slowly than ordinary powder, and thus produces a gradual and sustained effect upon the projectile. It is said that the smoke produced disappears with extraordinary rapidity, probably owing to the solution of the solid products in the relatively large proportion of water produced, in the form of vapor, on explosion.

Gun-cotton and nitro-glycerine produce little or no smoke when fired. Owing to the difficulty of controlling or retarding the sudden combustion of these substances, however, they have never been successfully adapted for use in fire-arms, in spite of the large amount of patient experiment which has been expended upon this problem.

The first nearly smokeless powder was probably that introduced by Colonel Schulze, of the Prussian Artillery. This consisted of small particles of wood, purified, partially converted into nitro-cellulose, and mixed with potassium chlorate. Within a few years much interest has been aroused by the report that the French government had secured the secret of a perfect smokeless explosive, called the "Vieille powder," or *poudre B.* It is now known that this was a compound of picric acid; it has been supplanted by later discoveries.

The invention of *blasting gelatine*, by Nobel, in 1875, opened the way to the successful application of such powerful explosives as nitro-glycerine and gun-cotton to military purposes. Nitro-glycerine, as is well known, contains an excess of oxygen over that required to completely burn the carbon and hydrogen contained in it, while gun-cotton shows a slight deficiency. Blasting gelatine is a translucent, elastic substance, made by dissolving about eight parts of nitro-cotton in ninety-two parts of nitro-glycerine. The nitro-cotton is a lower degree of nitration of cellulose, similar to collodion cotton. This new explosive is unaffected by water, does not readily explode by percussion, and when detonated explodes with an energy greater than that of either of its constituents. By suitable additions of inert material the rapidity of its explosion may be moderated, and its usefulness for blasting purposes thus greatly increased. This may also be effected by increasing the proportion of nitro-cotton, and in this way a mixture suitable for the ordinary uses of gunpowder may be obtained. The most successful modern "smokeless powders" are of this character.

Nobel's smokeless powder, "balistite," consists of about equal parts of nitro-glycerine and soluble nitro-cotton, with the addition of a small proportion of camphor for the purpose of bringing about the combination of the materials; the effect of the camphor

is also to greatly moderate the violence of the explosion. Another smokeless powder, "cordite," invented by Abel and Dewar, is a similar mixture of nitro-glycerine and ordinary gun-cotton, the combination of the two being brought about by the aid of acetone or other solvents; camphor or tannin is added to reduce the rapidity of the explosive action. These powders are similar to blasting gelatine in appearance, and are used in the form of small cubical grains. They are even more gradual in their action than gunpowder, and the rapidity of explosion can be modified to any desired degree by the addition of suitable proportions of camphor, etc. These powders are almost absolutely smokeless, and seem to be capable of successful use in small-arms or cannon. Experiments are now being carried on by several governments with a view to testing the efficiency of the new explosives, and determining the methods by which they can be most safely stored, transported and handled.

SPENCER B. NEWBURY.

STEREOCHEMISTRY.[1]

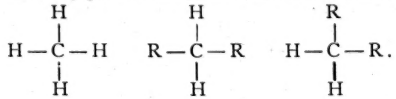
I.—*The Stereochemistry of Carbon.*

It is only seventeen years since the theory of geometrical isomerism first took definite form. Yet the study of structural isomerism dates from 1824, and in 1830 the comparison of tartaric with racemic acid brought even Berzelius to admit that substances of like composition could have unlike chemical properties, and caused him to propose the term isomerism for such cases. The conception of isomerism was that of compounds containing the same elements in the same proportions and yet differing in properties; the difference being due to the different grouping of the elements in the different compounds. The conception of geometrical isomerism is that of compounds containing the same elements in the same proportions and arranged in the same groups, and yet differing in properties; the difference being due to the different arrangement in space of the constituent groups of the several compounds. The second conception is thus a natural outgrowth of the first. The growth seems not great; the time required for it—more than forty years—seems at first sight disproportionately long. But in this time much had to be done. The first conception has for its basis a knowledge of composition, quantitative as regards the elements present. Identity of composition proven, difference of grouping was inferred; and under the stimulus of the radicle-theory and its successors the work of testing compounds, among others isomeric compounds, for the presence or absence of certain groups went on rapidly. But this qualitative detection of groups was not enough: the second conception has

[1] Based on lectures delivered at Cornell University.

for its basis a knowledge of composition, quantitative as regards the groups present. To prove the structural identity of two molecules it was not enough to show that every group which had been found in one might also be detected in the other; it had to be shown that the whole structure of each molecule was expressed by its division into these groups; that no difference in sub-grouping due to structural isomerism within the primary groups was possible. Thus only in 1873 was it possible for Wislicenus, by demonstrating that the groups CH_3, OH, CH, and COOH were present in sarcolactic, as well as in ordinary lactic acid, to prove the structural identity of these acids. On this proof was based the dictum of Wislicenus: "The facts compel us to explain the difference between isomeric molecules having the same structural formulæ by the different arrangement of their atoms in space." "Words," says Van't Hoff,[1] "which I wish to quote because they set me thinking" ("ils m'ont mis à réfléchir sur le problême en question"). It was, then, a comparison of the number of isomers derivable from an ordinary structural formula with the number derivable from a formula representing "the arrangement of the atoms in space" that led Van't Hoff to the conception of his theory.

For the ordinary formulæ represent the atoms as if they all occupied the same plane. Now the number of isomers CH_2R_2 derivable from any plane-formula for CH_4 is two or more:



The only arrangement which excludes the possibility of isomerism is an arrangement in which all the hydrogen-atoms are equidistant from one another as well as from the carbon-atom; an arrangement possible only in three dimensions (Fig. 1).

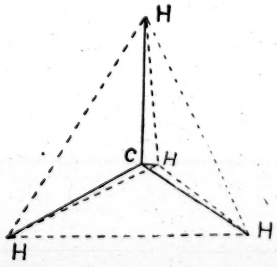


FIG. 1.

[1] "Dix années dans l'histoire d'une théorie" (Rotterdam, 1887), p. 24.

Thus the single fact that only one CH_3R_1 can exist compels us to adopt for CH_4 a three-dimensional formula—to suppose that the hydrogen-atoms are arranged round the carbon-atom as the corners of a regular tetrahedron round the center of it.[1] This conception had already been embodied in the carbon-model of Kekulé.

The Theories of Van't Hoff and of Le Bel.

But Van't Hoff went farther and, noting that this formula admits of isomerism only in one case, viz. when a different radicle occupies each corner of the tetrahedron, he recognised the peculiarity of this isomerism:

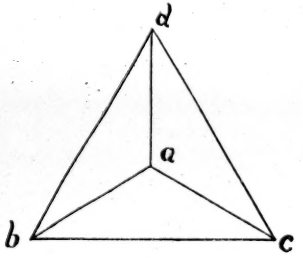


FIG. 2.

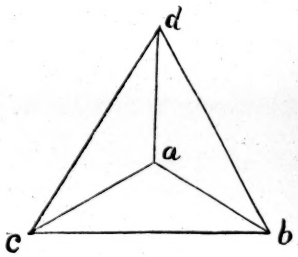


FIG. 3.

that it depends only on the order in which the groups are arranged, and that the isomers bear to one another the relation of object and image (Figs. 2 and 3).[2] On account of the lack of symmetry imparted to a regular tetrahedron by making every corner of it different, Van't Hoff called a carbon-atom combined with four different radicles an asymmetric carbon-atom (henceforth written *C*).

For proof that the peculiar isomerism demanded by his formulæ

[1] Such was the reasoning relied on by Van't Hoff and universally accepted as sound until last year, when Le Bel published a remarkable paper on "The conditions of equilibrium of the saturated compounds of carbon" (Bull. Soc. Chim. [3] **3**, 788). The assumption underlying the argument just given is that when CH_3R is formed from CH_4, R takes the place of one of the H atoms; an unwarranted assumption, says Le Bel, for the position (or positions) of equilibrium of the system CH_3R depends on the particular properties of the elements of which this system is composed, and not on the position which the elements may have occupied in the system CH_4. That each of these systems has only one position of equilibrium tells us nothing as to the configuration of either; the hydrogen atoms of CH_4 may be quite irregularly disposed, and yet the number of compounds CH_3R may not exceed one. Le Bel points out, however, as Wislicenus did, in the second edition of his treatise (p. 78), that the crystal-forms of most substances of the type CR_4 indicate that their molecules have the symmetry of the regular system. So that the symmetrical tetrahedral configuration of these substances is a result of observation, though, as has been shown, not a theoretical necessity.

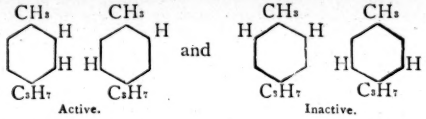
[2] It is only for convenience that Van't Hoff represents *C a b c d* by a regular tetrahedron—a figure which really represents only such compounds as Ca_4, for difference among the radicles involves inequality of the forces connecting them with carbon and with one another; hence the distances *Ca*, *Cb*, *Cc*, *Cd* are all different, and *C a b c d* is properly represented by a tetrahedron quite irregular. This is important when we have to consider the interaction of radicles attached to two linked tetrahedra.

really existed, Van't Hoff pointed to the right-handed and left-handed modifications of substances which rotate the plane of polarised light; to the fact that this property of rotation is in the case of solutions peculiar to substances which contain *C*, and to the fact that the relation between his formulæ for the two modifications—the object-and-image relation—is identical with the relation between the crystal-forms of the two modifications.

Van't Hoff published his theory in Dutch in September, 1874;[1] Le Bel's paper on the same subject appeared in November, 1874.[2] A number of cases of unexplained isomerism had led Van't Hoff to his theory of optical activity. With Le Bel the attempt to account for optical activity led to the suggestion of three-dimensional formulæ, and so to a consideration of the number of isomers deducible from such formulæ. Not the chemical researches of Wislicenus, but the physical phenomena observed by Pasteur, Rammelsberg and Reusch, and accounted for theoretically by the mathematics of Sarrau, formed his starting point. For these established the coincidence of rotatory power in *solids* with a certain characteristic arrangement of their *particles*—an arrangement characteristic in its lack of symmetry—the lack of symmetry being complementary in the case of the two forms of a substance which rotate to the right and to the left respectively, so that while it suffices to prevent superposition of the two forms, it leaves each the mirrored image of the other. And Le Bel supposed that in the case of substances which are optically active when *in solution*, this complementary asymmetry must exist in the arrangement of the *atoms* in the molecule. The usual statement (Victor Meyer,[3] v. Richter,[4] Pattison Muir,[5]) of Le Bel's theory is that he, as well as Van't Hoff, maintained that every substance optically active in solution contains *C*. What Le Bel[6] maintained was that "in general if a substance is derived from our primitive type MA_4 by the substitution of three different atoms or radicles for A_4, its molecule will be asymmetrical and will possess the power of rotation." "Thus, if in the formula of a substance we find carbon combined with three monatomic radicles differing from one another and from hydrogen, the substance should be active" (p. 339). This is the converse of the usual statement. Further, since "M is a radicle simple or complex" (p. 338), it is *not* necessarily a single carbon-atom to which the four unlike groups must be attached to cause rotation. This is the reverse of the usual statement. The importance of reversing it is not merely historical, as will be seen later.[7] Le Bel, then, gave the case of a tri-substituted methane as only one example of the application of a principle. Ethylene derivatives might or might not prove to be optically active accord-

[1] "Dix années," etc., p. 13.
[2] Yet Pattison Muir, in his "Principles of Chemistry," ascribes the Van't Hoff-Le Bel theory to "Van't Hoff following Le Bel in 1875" (p. 181), to "Van't Hoff following in the steps of Le Bel" (p. 304, 2d ed.).
[3] Ber. d. chem. Ges. **23**, 574.
[4] Organische Chemie, p. 47.
[5] Loc. cit., p. 304.
[6] Bull. Soc. Chim. **22**, 338.
[7] Comp. Herrmann: Ber. d. chem. Ges. **21**, 1949.

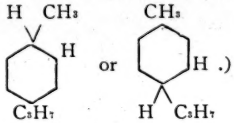
ing as the hydrogen-atoms were or were not in the same plane. Tri-substitution products of benzene should be active. The asymmetry of the whole molecule, not the asymmetry of the groups attached to any one carbon-atom in it, was the criterion. Thus the formulæ of the terpenes would be



Active. Inactive.

(This hypothesis was based on the assumption that the methyl and propyl groups do not occupy a plane of symmetry of the whole molecule, as would be the case if all the atoms of the terpenes were in the same plane as shown.)

Van't Hoff's theory, on the other hand, was that every substance active in solution—benzene-derivative or not—contains *C*. In every case in which the constitution of such a substance has been determined, this statement is borne out. (Thus the formula of an active terpene can be only



.)

And Fock[1] has recently tried to show in detail the connection between *C* and the rotation of light. If of the radicles *a b c d* connected with *C*, $a>b>c>d$, then any rotation of these radicles will take place round the heaviest radicle *a* as axis, and more readily in the direction *bcd* than the other way. For *d*, the smallest radicle, is the thin end of the wedge (Fig. 4). Fock

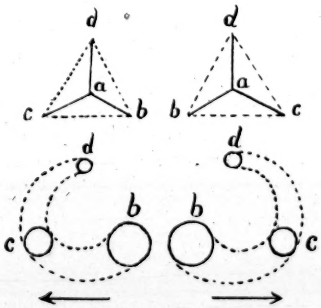
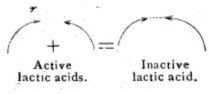


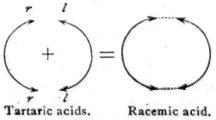
FIG. 4.

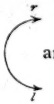
[1] Ber. d. chem. Ges. **24**, 101; compare Ostwald's criticism, Ztschr. phys. Chem. **7**, 429. See also the theory of Guye, Bull. Soc. Chim. [3] **3**, 595

shows how such rotation would account for optical activity and for the way in which it is affected by solvents.

The converse of Van't Hoff's theory, the statement that every *C* group is optically active, has received confirmation in so many instances that it now has the support of Van't Hoff. This does not imply the belief that every *substance* containing *C* is optically active. A substance may contain molecules of equal and opposite activity in equal numbers, as in the case of racemic acid and of ordinary inactive lactic acid, the zinc salt of which has recently been made synthetically from the zinc salts of the right-handed and left-handed acids.[1]

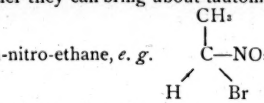
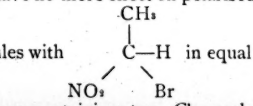


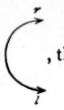
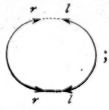


Nor is the belief implied that every *molecule* containing *C* is optically active. The molecule may be divided against itself, possessing *C* groups of equal and opposite activity in equal numbers, as is the case with mesotartaric acid,  and probably with erythrite, $\begin{matrix}CH_2OH\\CHOH\\CHOH\\CH_2OH\end{matrix}$, which yields mesotartaric acid on oxidation. Substances containing only one *C* are, of course, excluded from this latter class, and all such substances should either be active or resolvable into two compounds of equal and opposite activity. "And in fact," says Van't Hoff,[2] "to this day no inactive substance of this class has resisted decomposition." "Fourteen times the 'doubling' has been attempted and the attempt has never been in vain."[3] But the usual methods of "doubling": the action of living organisms, which decompose one of the active isomers faster than the other; and the combination of the inactive with an active body, cannot always be applied. Easterfield[4] found this to be the case with chlor- and brom-phenyl-acetic acids, which proved to be inactive even when formed from active mandelic acid. Indeed, the only active substance containing a halogen linked with *C* is amyl iodide, $C_5H_5-\overset{H}{\underset{I}{C}}-CH_3$. And

[1] Schardinger: Monats. für Chem. **11**, 558.
[2] "Dix années," etc., p. 43.
[3] Loc. cit., p. 45.
[4] J. Chem. Soc. **59**, 71 (1890).

of substances containing fewer than three carbon-atoms not one is known to be active though many contain *C*.[1]

Victor Meyer, in his interesting review of stereochemistry,[2] has proposed an explanation of this fact. Simple groups, it is said, are more mobile than complex ones; hence by changing places with one another they can bring about tautomerism. And molecules of brom-nitro-ethane, *e. g.*  in which the hydrogen-atom and, say, the nitro-group are constantly changing places, would have no more effect on polarised light than a mixture of such molecules with  in equal numbers.

For substances containing two *C*'s, each combined with the same groups, two inactive forms are possible: one of the meso-tartaric type  , the other of the racemic type  ; but only the former should be non-resolvable. Some substances, however, as dibrom-succinic acid[3] and hydrobenzoin, exist in two inactive forms, neither of which has yet been resolved. While

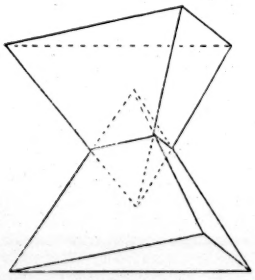


FIG. 5.

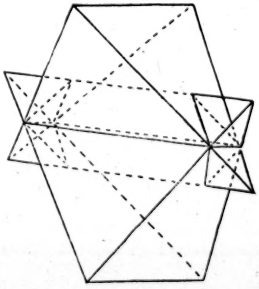


FIG. 6.

[1] Landolt: "Handbook of the Polariscope." Translated by Robb and Veley (London, 1882), p. 29. Tables showing the relation between optical activity and composition are given.

[2] Ber. d. chem. Ges. **23**, 567.

[3] Attempts at doubling derivatives of succinic acid which contain *C* are now in progress. Bischoff and Walden: Ber. d. chem. Ges. **23**, 1957.

then the original statement of Van't Hoff that every substance active in solution contains *C* is proved without exception, the converse theory that every *C* shows optical activity except when this is neutralised by the activity of another *C*, requires further proof. Meanwhile no fact incompatible with it is known.

The extension of Van't Hoff's space-formulæ from a single carbon-atom to two combined carbon-atoms was simple. "The very fundamental principle of the tetrahedral arrangement demands that two carbon-atoms singly-linked shall occupy at once the center of one tetrahedron and the apex of the other."[1] (Fig. 5.) From this arrangement that for two doubly-linked carbons is deduced. (Fig. 6.)

It is now usual to represent singly-linked carbons by tetrahedra having an apex in common, the doubly-linked tetrahedra having an edge in common; this is simpler, and has so far sufficed to represent the facts.

In a substance of the formula $CR^1R^2R^3R^4$ the distances separating the groups in the right-handed form are the same as in the left-handed form. Hence the resulting isomers are characterised by physical rather than by chemical differences. Another kind of isomerism results, however, from the arrangement of the R-groups in $C_2R^1R^2R^3R^4$. Here also two space-formulæ exist for any one structural formula, $\begin{matrix} CR^1R^2 \\ \| \\ CR^3R^4 \end{matrix}$, viz. Fig. 7 and Fig. 8.

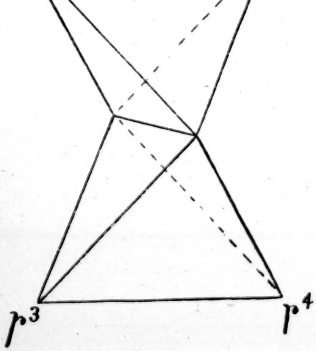


FIG. 7.

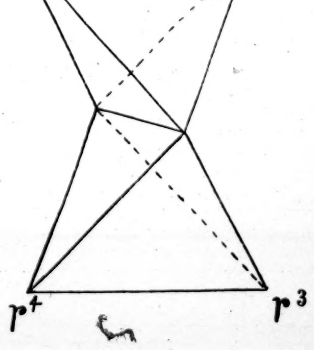


FIG. 8.

[1] Loc. cit., p. 52.

In Fig. 7 R^1 and R^3 are nearer together than in Fig. 8; the same is true for R^2 and R^4. Hence isomers of this type will be characterised by chemical differences. This isomerism will exist also for substances of the type $\begin{matrix}CR^1R^2\\ \|\\ CR^1R^2\end{matrix}$ $\left(=\begin{matrix}R^1CR^2\\ \|\\ R^1CR^2\end{matrix}\right.$ and $\left.\begin{matrix}R^1CR^2\\ \|\\ R^2CR^1\end{matrix}\right)$, and of the type $\begin{matrix}CR^1R^2\\ \|\\ CR^1R^2\end{matrix}$ $\left(=\begin{matrix}R^1CR^2\\ \|\\ R^1CR^2\end{matrix}\right.$ and $\left.\begin{matrix}R^1CR^2\\ \|\\ R^2CR^1\end{matrix}\right)$, but not for $\begin{matrix}C(R^1)_2\\ \|\\ CR^2R^3\end{matrix}$, since $\begin{matrix}R^1CR^1\\ \|\\ R^3CR^3\end{matrix} = \begin{matrix}R^1CR^1\\ \|\\ R^2CR^2\end{matrix}$. To show that the number of isomers foreseen by this theory is in accord with the facts we may cite the testimony of an opponent[1] of the theory, to the effect that substances possessing the same structural formulæ and containing two doubly-linked carbons united to different groups will exist in two isomeric forms. More than thirty such substances (besides derivatives), all presenting this isomerism, may be counted: among them are fumaric and maleïc acids, the crotonic and the cinnamic acids.[2]

ARNOLD EILOART.

(To be continued.)

SOLUTIONS. By W. OSTWALD, Professor of Chemistry in the University of Leipzig. Being the fourth book of the second edition of Ostwald's "Lehrbuch der allgemeinen Chemie," with some additions. Translated from the German by M. M. PATTISON MUIR. Longmans, Green & Co.: London and New York, 1891.

A translation of even a portion of Ostwald's great "Lehrbuch" will be welcomed by all who use English with more ease than German. The work of translation, by Mr. Muir, is excellent. His style is clear and scholarly throughout. The accuracy of the translation is insured by the fact that Ostwald has revised the proofs of the English edition.

The object in offering this work to the public, as stated in the author's preface, is that "there are always objections to publishing a part of a book, but in the present case the issue of a part of a larger book seems to be justified by the consideration that a comprehensive survey of the very remarkable advances, both theoretical and practical, which have been made in the last few years in the subject of solutions must be useful to all who are not in a position to make themselves acquainted with the many and widely-scattered memoirs on this subject."

The most prominent characteristic of the entire "Lehrbuch der allgemeinen Chemie" is the importance attached to the physical side of chemistry. This feature is very pronounced in this

[1] Michael, Ber. d. chem. Ges. **30**, 550.
[2] Liebermann, Ber. d. chem. Ges. **23**, 2510, describes a third cinnamic acid not accounted for by the theory.

volume of 316 pages, which is almost entirely devoted to the discussion of the physical phenomena presented by solutions.

The book is divided into ten chapters. Chapter I. treats of solutions in gases. Chapter II.—Solutions of gases in liquids. Chapter III.—Solutions of liquids in liquids. Chapter IV.—Solutions of solids in liquids. Chapter V.—Osmose. Chapter VI.—Diffusion. Chapter VII.—Vapor-pressures of solutions. Chapter VIII.—Freezing-points of solutions. Chapter IX.—Salt-solutions. Chapter X.—Simultaneous action of several solvents.

This translation has appeared at an opportune moment. As is well known to readers of chemical literature, an active discussion has been carried on as to what takes place when one substance dissolves in another. The view that in solution the substance dissolved breaks down into simpler parts, the molecules themselves decomposing into their "ions," is held by such men as Van't Hoff, Arrhenius and Ostwald. A systematic treatise on this subject is furnished by this work on "solutions," and the book can be heartily recommended to all who are interested in one of the leading scientific discussions of to-day. H. C. J.

REPETITORIUM DER ORGANISCHEN CHEMIE. Von Adolf Pinner. Berlin, 1890.

Prof. Adolf Pinner has prepared a new edition of his excellent "Review of Organic Chemistry." Its popularity is shown by the fact that this is the ninth edition since 1872, and the popularity is deserved. The book is written for chemists beginning the study of chemistry, and for students of medicine and pharmacy. It differs for the better from most of its German rivals in two points. Under the title "methyl compounds," the halogen, hydroxyl, thio, nitrogen, and metal, substitution-products of methane are successively fully discussed, with constant reference to analogies with inorganic compounds; then the corresponding derivatives of ethane are taken up, followed by those of the other hydrocarbons in order. The aromatic series is treated similarly. There can be little doubt that this system is the best in a book which is intended for beginners, and which, hence, can omit mention of many compounds. And herein lies the second advantage of Prof. Pinner's book; while it is full enough, explaining clearly most compounds of practical or theoretical interest, and showing their relations to simpler forms, it attempts no more. The summaries at the end of the different sections are helpful to students. An appendix contains a few pages on stereo-chemistry, on analytical and synthetic methods, on methods for determining constitution and molecular weight, but, singularly enough, makes no mention of the methods of Raoult or Beckmann, which, surely, are simple and important enough to be explained to the student at the close of his course. E. R.

A HISTORY OF CHEMISTRY, FROM EARLIEST TIMES TO THE PRESENT DAY. By Ernst von Meyer. Translated, with the author's sanction, by George M'Gowan, Ph. D., Demonstrator in Chemistry, University College of North Wales, Bangor. London: Macmillan & Co., 1891.

Prof. v. Meyer's "Geschichte der Chemie" has already been reviewed in this place;[1] it remains but to notice the appearance of the work in English. The fact that Dr. M'Gowan has been a pupil of the author, and that he has already been acknowledged a successful translator, would argue in favor of the value of this book; moreover, the proof-sheets, it is stated, have been revised by Prof. v. Meyer himself.

The style of the original is closely followed throughout, indeed in some ways the book suffers from being a too literal translation. In places Dr. M'Gowan's endeavor to be accurate involves him in the use of expressions which are more German than English, as, for example, in the rendering of compound substantives. This slight defect should not, however, be taken into account, in view of the many excellences which the work evidently possesses.

W. W. R.

OBITUARY NOTICE.

Dr. VICTOR VON RICHTER, Professor of Chemistry in the University of Breslau, died suddenly October 8. He was born in 1841; studied physics and chemistry at Dorpat, and from 1862 to 1872 was assistant to Mendelejeff in the Technological Institute at St. Petersburg. For a time he was also a teacher in the University of St. Petersburg. In 1872 he accepted a call to the Academy of Agriculture and Forestry at Nowo-Alexandria in Poland. In 1874 he became "Privatdocent" in the University of Breslau, after having spent some time at Bonn with Kekulé. In 1879 he was made professor (*extraordinarius*) in the University, and last year he became professor (*extraordinarius*) of technical chemistry in the new Technological Institute at Breslau.

Richter was widely known for his investigations in the field of organic chemistry, but his name is most familiar as that of the author of the well-known text-books, "Lehrbuch der anorganischen Chemie" and "Chemie der Kohlenstoffverbindungen." Six editions of each of these books have been issued in Germany. They have, further, been translated into English, Dutch, and Italian, and the "Lehrbuch der anorganischen Chemie" into Russian. By these books Richter has contributed materially to the advance of chemistry during the last fifteen years.[2] I. R.

[1] This Journal **11**, 429.

[2] For a fuller account of Richter see Chemiker Zeitung **15**, No. 82, p. 1495, October 14, 1891.